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VOLUME 26 JULY 26, 1937 NO. 15

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uarterly Research Number

AMERICAN

DYESTUFF REPORTER

A. P. HOWES
Publisher

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Official Publication of the American Association of Textile Chemists and Colorists

THE OBJECTS OF THIS ASSOCIATION ARE:

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PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

JULY 26, 1937

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AMERICAN DYESTUFF REPORTER

Official Journal

With the present issue of the AMERICAN DYESTUFF REPORTER we are inaugurating a new departure.

For the convenience of our readers, particularly members of the Association, we are bringing together in one issue, (which we will from now on designate as the Quarterly Research Number) reports on research projects and other experimental work in which the Research Committee of the A.A.T.C.C. is engaged. By this method of publication most of the research reports will be found in four numbers which will be published in January, April, July and October, and as a result members will only have to look through four issues of the REPORTER to locate the more important publications of the Research Committee.—L.A.O.

State of the Sulfur in Oxidized Wool

MILTON HARRIS and ARTHUR SMITH*

During treatment with oxidizing agents, the disulfied sulfur in wool appears to be changed to higher states of oxidation. The existence of oxidation derivatives of the disulfide compounds is indicated by the alkali-solubility determination, the lead acetate test, by reduction with hydrochloric acid-potassium iodide solutions, and by cystine analyses.

The intermediate oxidation derivatives of cystine are unstable under the conditions necessary for protein hydrolysis, and at least one of them, cystine disulfoxide, is partially converted to cystine. The results indicate that the values obtained for the cystine content of oxidized wool may be expected to be higher than the actual cystine content since they represent the amount of cystine formed from the partially oxidized compounds as well as from unoxidized cystine groups.

I. INTRODUCTION

RECENT investigations relating to the oxidation of wool[1, 2, 3, 4] indicate that the stability of the fiber is closely related to the state of the sulfur in the wool protein. The bulk of the sulfur in untreated wool is present as cystine sulfur[5, 6] and it appears that the maximum stability of the fiber is obtained when the sulfur is in this form. Changes in the state of this sulfur, such as are produced by oxidizing and reducing agents or by light, may result in the direct degradation of the fiber, or in incipient damage, which may be greatly aggravated in the subsequent processing of the fiber. It is apparent, therefore, that the proportion of the total sulfur in wool which exists in the disulfide form is very significant.

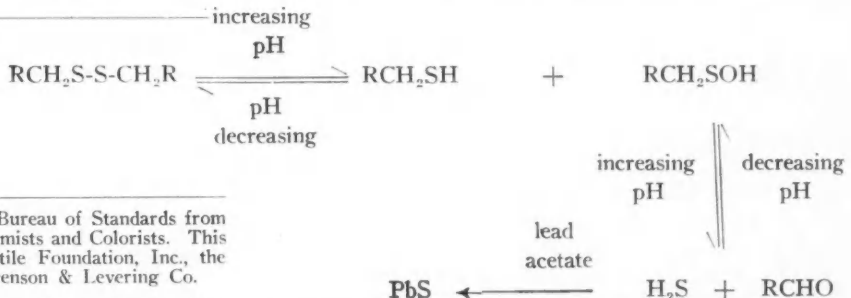
The present report is concerned with new methods which have been used in studying the state of the sulfur in oxidized wool and with the limitations of the methods for the determination of cystine when applied to wool in which the sulfur has been changed to a higher state of oxidation.

II. THE STATE OF THE SULFUR IN OXIDIZED WOOL

When wool is treated with oxidizing agents, one of the main points of attack appears to be the disulfide linkage. Intermediate oxidation products such as R-SO-S-R, R-SO_2-S-R, etc., may be formed†. Although methods for the identification of the individual intermediate oxidation derivatives of sulfur are not known, evidence given by four different methods indicates that the disulfide sulfur in wool is changed to higher states of oxidation during treatment with oxidizing agents. These tests are the alkali-solubility determination, the lead acetate test, the reduction method using mixtures of hydrochloric acid and potassium iodide, and the determination of the cystine content.

The alkali-solubility test[7] has been shown to be a measure of the extent to which wool is oxidized. Presumably as the number of oxygen atoms on the sulfur increases, the bond between the disulfide sulfur atoms becomes increasingly labile and more wool goes into solution. Analogous reactions are obtained with cystine and its intermediate oxidation derivatives. Cystine disulfoxide (RSO_2-SR or RSO-SOR) has been shown by Lavine[8] to be much less stable in alkaline solution than cystine whereas Toennies[9] has recently found cystine disulfone (RSO_2-SO_2R) to be even less stable than the disulfoxide.

The lead acetate test[2], which distinguishes between unbleached wool and wool bleached with hydrogen peroxide also appears to depend on the state of oxidation of the sulfur. When untreated wool is subjected to this test, hydrogen sulfide is liberated and reacts with lead acetate to form lead sulfide according to the following scheme:



Cystine appears to react similarly but requires a higher pH for formation of the lead sulfide. Oxidized wool and cystine disulfoxide, on the other hand, do not form lead sulfide under the conditions in which it is formed in untreated wool and in cystine.

*Research Associates at the National Bureau of Standards from the American Association of Textile Chemists and Colorists. This work is aided by grants from the Textile Foundation, Inc., the Chemical Foundation, Inc., and the Eavenson & Levering Co.

†One sulfur atom in a disulfide compound is positively and the other negatively charged. It would be expected that only the positive sulfur would take up oxygen until it formed a sulfonic acid, the bond between the sulfur atoms then being broken. The remaining sulfur could then be oxidized to a sulfonic acid. This mechanism appears to be more tenable than one in which there is simultaneous oxidation of both sulfur atoms, with the formation of such intermediates as R-SO-SO-R, R-SO_2-SO-R, etc.

The following mechanism is suggested for those cases in which the disulfide sulfur has been partially oxidized. Since in each disulfide group one sulfur atom is positively and one negatively charged, the negative oxygen atoms or hydroxyl groups react with the positive sulfur, whereas the positive groups such as hydrogen react with the negative sulfur. The hydrolytic cleavage of a partially oxidized disulfide compound may then be represented as follows:

$$(1)\ \text{RSO-SR} \xrightarrow{H_2O} \text{RSO.OH} + \text{RSH}$$

The products of this reaction appear to be stable under the conditions of these experiments and further decomposition to form hydrogen sulfide does not occur.

The third method is based on the method used by Lavine[8] in his studies on cystine disulfoxide. Samples of oxidized wool were treated for 1 hour with mixtures of equal volumes of solutions of 4 *M* hydrochloric acid and 4 *M* potassium iodide, the ratio of wool to solution being 1 to 100. The reductions were conducted in the dark at 22-23° C. The oxidizing value of some of the intermediate oxidation products was determined by direct titration of the iodine liberated with sodium thiosulfate. The value obtained has no quantitative significance with respect to the extent of oxidation of the wool since, as has been shown by Lavine, only sulfur which has been oxidized below the sulfonic acid state is reduced.

The cystine content of wool has been shown[1] to decrease with increased oxidation. That the values for the cystine content of oxidized wool have no quantitative significance will be shown later.

Of the four methods described, the alkali-solubility test is the most satisfactory. A comparison of the results obtained by the different methods is given in Table 1.

III. THE DETERMINATION OF CYSTINE IN OXIDIZED WOOL

The available methods for the estimation of disulfide compounds have been classified and evaluated elsewhere[10] and need not be further discussed here. In the work reported in this paper, cystine was determined by the methods of Sullivan[11], Okuda[12], and Folin-Morenzi[13]. The latter two were used as described in the literature, while the Sullivan procedure was modified only with respect to the measurement of the color developed in the determination. A few interesting points regarding this procedure are here noted.

The amount of the colored substance developed by the reaction of cysteine with sodiumβ-naphthoquinone-4-sulfonate was measured photometrically at the wave length 501 millimicrons. A calibration curve, shown in Figure 1, was obtained by determining the transmittancy of the red solutions formed when known amounts of cystine were treated according to the Sullivan procedure.

When this method was first used, erratic results were obtained, especially during the summer when the temperature rose above 30° C. It was found that the reaction is markedly affected by temperature as shown in Figure 2. The initial rate of development of color increases with increasing temperature but at equilibrium, the amount of colored substance developed decreases with increasing temperature. Analyses of solutions containing 100 mg. of cystine per liter were made, the color being allowed to develop at different temperatures for 30 minutes. The results are shown in Figure 3. There is practically no change between 24 and 30° C. but above 30° C, the apparent cystine content decreases rapidly with increasing

TABLE 1

The Effect of Treatment for Different Lengths of Time With Hydrogen Peroxide on the Sulfur in Wool. The Alkali-solubility and Cystine Contents were Determined on Wool Which Had Been Treated at 50° C. with 0.6% (2 vol.) Hydrogen Peroxide While the Remaining Two Tests Were Made on Wool Similarly Treated Except That 3% (10 vol.) Peroxide was Used

Duration of treatment	*Alkali-solubility*	*Cystine content*	*Lead-Acetate test**	*Hydrochloric acid-potassium test†*
hrs.	*per cent*	*per cent*		*milli-equivalent of iodine per gram of wool*
0	9.7	11.6	positive	0
1	10.3	10.7	negative	.015
3	12.4	10.1	negative	.024
5	15.2	10.0	negative	—
7	18.2	9.85	negative	.038
9	20.1	9.58	negative	.051
16	40.0	8.63	negative	.072

*These results are obtained visually. The lead sulfide formed in the reaction darkens the wool.

†Similar experiments with oxidized silk showed no significant changes in iodine liberated with increased oxidation.

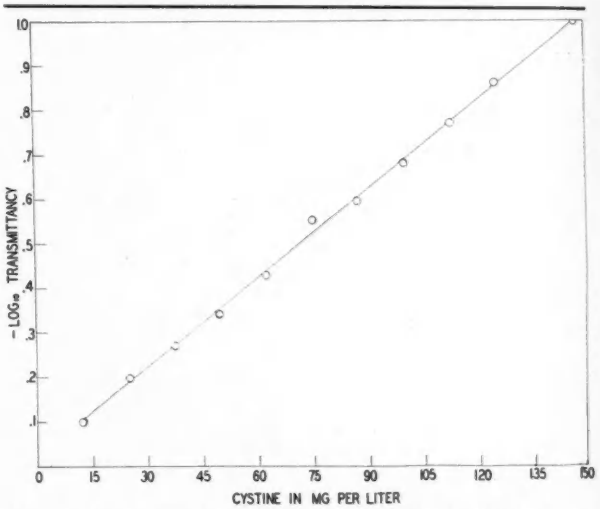


Fig. 1—The Transmittancy at Wave Length 501 Millimicrons of the Red Solutions Formed When Known Amounts of Cystine Were Treated According to the Sullivan Procedure.

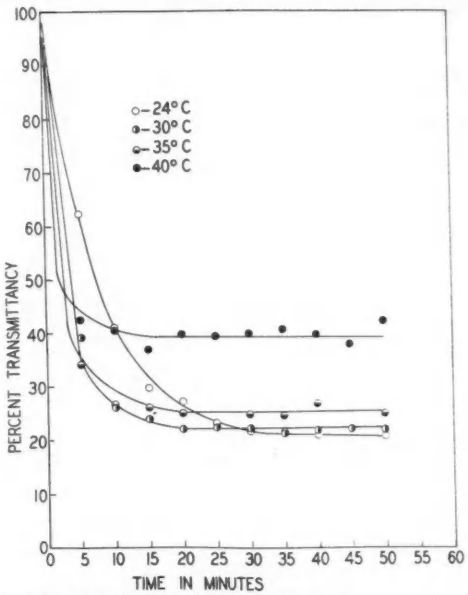


Fig. 2—The Effect of Different Temperatures on the Rate of Color Development in the Sullivan Method for the Determination of Cystine.

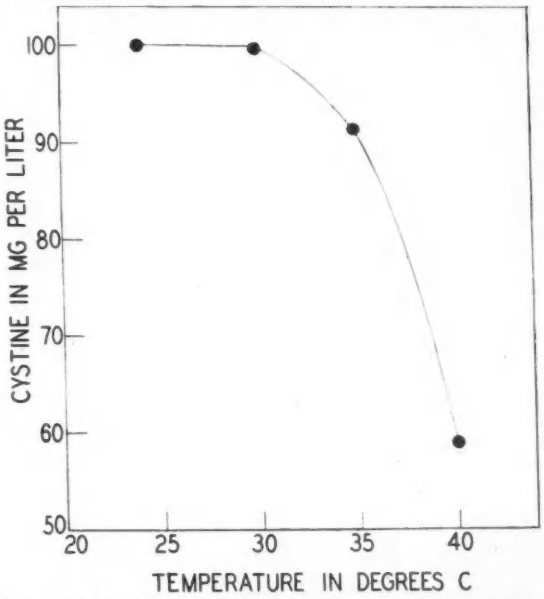


Fig. 3—The Effect of Temperature on the Apparent Cystine Content of Solutions containing 100 mg. of Cystine per Liter.

temperature. The cystine determinations reported in this paper were made at 23-24° C.

Analyses of six samples of the untreated wool used in this work showed an average cystine content of 11.5 per cent with an average deviation from the mean of 0.2 per cent.

The lability of the intermediate oxidation derivatives of cystine, shown by Toennies[9] and Lavine[8], suggested that similar derivatives formed in wool during oxidation might partially revert to cystine during the hydrolytic process which is used in the analyses of proteins for cystine. In order to test this possibility, 10-mg. samples of cystine disulfoxide* were treated with 5 ml. portions of 6 *N* hydrochloric acid in an oil bath at 120-5° C. for different lengths of time, and the amount of cystine in the resulting solutions was determined by the Sullivan and the Okuda methods. A similar set of experiments, using 6 *N* sulfuric acid, was made and the cystine determined by the Folin-Morenzi method. The results recorded in Table 2 show that one mole of cystine is formed from two moles of cystine disulfoxide.

The results of the above experiments indicate that under the conditions necessary for the hydrolysis of proteins, at least a portion of the oxidized disulfide groups revert to disulfide groups. Therefore the values obtained for the cystine content of oxidized wool may be expected to be higher than the actual cystine content since they represent the amount of cystine formed from the partially oxidized cystine compounds as well as from unoxidized cystine groups.

*The cystine disulfoxide used in this work was furnished by Drs. Toennies and Lavine of the Lankeman Hospital Research Institute, Philadelphia, Pa.

TABLE 2

The Decomposition of cystine disulfoxide During the Hydrolysis Used in Cystine Analyses. The values Represent the Mole Per Cent of the Cystine Disulfoxide Which Has Been Converted to Cystine

Duration of hydrolysis	*Cystine found*		
	Sullivan	*Okuda*	*Folin-Morenzi*
hrs.	*per cent*	*per cent*	*per cent*
1	46.5	53.8	45.7
3	48.3	54.6	50.0
5	46.1	52.0	47.5
7	48.6	54.3	47.0
10	47.5	45.8	45.8
20	52.0	56.4	46.7
50	45.3	52.4	49.1
75	52.3	51.4	48.2

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Nature of the Acid-Dyeing Process

ARTHUR SMITH and MILTON HARRIS*

The dye-combining capacity of untreated wool has been determined for the typical acid dye, orange II, and shown to be equal to the acid-combining capacity. Treatments with nitrous acid, hydrogen peroxide, sodium hypochlorite, and strong solutions of sulfuric acid decrease the basicity of the wool and correspondingly decrease the affinity for acid dyes. Chlorinated wool absorbs acid dyes at a greater initial rate than untreated wool, but at equilibrium the latter absorbs more dye. The resist to acid dyes produced in the sulfuric-acid-carbonizing process is caused by the conversion of basic amino groups to sulfamic-acid derivatives. The results of the investigation constitute further evidence in favor of the chemical theory of acid dyeing.

I. INTRODUCTION

THE complexity of dyeing processes has given rise to many theories, all of which may be classified under the general headings of chemical or physical. However, the more recent work of Elöd[1], Porai-Koschitz[2], Speakman[3], and their collaborators leaves little doubt that the reaction of wool with acid dyes is governed by chemical laws and consists in the neutralization of the basic groups in the fiber by the acidic groups of the dye molecules. The data in the present report, obtained by a somewhat different approach to the problem, constitute further evidence in favor of the chemical theory for this type of dyeing.

II. ACID-DYE-COMBINING CAPACITY OF UNTREATED WOOL

The majority of the investigations relating to the mechanism of the acid-dyeing process have been made under conditions which closely approximate those used in the commercial dyeing of wool. Unfortunately, the amount of dye required for such a dyeing constitutes only a small fraction of the total dye which the wool is capable of absorbing and, as a result, data from such investigations have little quantitative significance.

Assuming that the acid-dyeing process consists in a reaction between the dye and the basic groups of the wool, then a given amount of wool should combine with equal molecular proportions of acid or acid dye. The acid-combining capacity of wool has been shown by several investigators[4, 5, 6, 7] to be about 0.80 millimole of acid per gram of wool and it has also been shown[8] that the combined acid may be accounted for by the free amino groups and by the quanidine nucleus of the arginine in wool. The acid-dye-combining capacity of the wool was determined in the present investigation by the following procedure. Yarn, prepared from wool which had been solvent-scoured, was further purified by extraction in a Soxhlet apparatus with alcohol and with ether, and finally was washed in water at 140° F. The dye was a purified sample of orange II, analysis of which showed 90.6 per cent of dye, 1.26 per cent of sodium chloride, and 8.15 per cent of moisture. The dyeings were boiled under a reflux condenser in a solution containing 1 millimole of dye per gram of wool, the ratio of wool to solution being 1:200. Sufficient sulfuric acid was added to obtain a pH of about 1.3, which is the pH shown by Elöd[1] to be necessary for the maximum absorption of acid dyes. The amount of dye absorbed from the solution was measured with a colorimeter by comparing the color of aliquots from the dye bath with that of solutions containing known amounts of the dye. The limiting absorption of dye appeared to be reached in 1.5 hours, when 0.85 millimole of dye per gram of wool had been absorbed. This value became slightly larger with increased time of dyeing, but on examination of the dye liquors, it was found that small particles of wool fibers were being split off.

This difficulty was readily overcome by lowering the temperature of the dye bath to 120° F., the only other effect being a considerable increase in the time necessary to reach equilibrium. The results of dyeing experiments at this temperature in a solution 0.1 N with respect to hydrochloric acid* are shown in Table 1. Equilibrium appears to be reached after about 12 hours. All subsequent dyeings were done under these conditions for 18 hours in order to be well within the equilibrium region.

The results of a similar set of equilibrium dyeings, using 0.5, 1.0, and 1.5 millimoles of dye per gram of wool are recorded in Table 2 and show that the amount of dye absorbed is independent of the concentration, providing sufficient dye is present to react with all of the basic groups in the fiber.

The values of 0.82 and 0.83 millimole of orange II absorbed per gram of wool are in good agreement with the

*Research Associates at the National Bureau of Standards, representing the American Association of Textile Chemists and Colorists. The work reported here was aided by grants from the Textile Foundation, Inc., Chemical Foundation, Inc., and the Eavenson & Levering Company.

*The pH of the dye bath was maintained with 0.1 N HCl, because in subsequent experiments, it was necessary to find out whether sulfuric acid was split off from wool which had previously been treated with concentrated solutions of sulfuric acid.

TABLE 1

Rate of Absorption of Orange II From a Solution at 120° F. Containing 1 Millimole of Dye per Gram of Wool, the ratio of wool to Solution Being 1:200. The Solution was 0.1 N With Respect to Hydrochloric Acid

Time Hours	*Amount of Orange II absorbed Millimole per gram of wool*
2	0.28
3.3	.38
5	.63
8	.71
9	.73
12	.81
21.3	.85
22	.82

TABLE 2

Effect of Varying the Concentration of the Dye Bath on the Amount of Dye Absorbed by Wool at Equilibrium

Concentration of Orange II in dye bath	*Amount of Orange II absorbed*
Millimoles per gram of wool	*millimoles per gram of wool*
0.50	0.49
1.00	.83
1.50	.82

acid-combining capacity and with the value 0.8 obtained by Porai-Koschitz[2] who used the dye eosine. He worked with the ammonium salts and showed that the amount of ammonia liberated corresponded to the amount of dye absorbed.

III. EFFECT OF VARIOUS TREATMENTS ON THE ACID-DYE-COMBINING CAPACITY OF WOOL

1. Effect of Nitrous Acid

One of the arguments that has been repeatedly used against the chemical theory of acid dyeing is based on what appears to be the unchanged affinity for acid dyes of wool treated with nitrous acid. Trotman[9], Paddon[10], and Benz and Farrell[11] attempted to destroy this affinity by deamination of the wool, and all concluded that treatment of wool with nitrous acid had little if any effect on the absorption of acid dyes by the fiber. All of these workers failed to realize that deamination, even when produced by prolonged treatment with nitrous acid, only partially destroys the basic properties of wool[3, 8]. In addition, they used amounts of dyes which would be readily taken up by the remaining basic groups in the wool.

More recently, however, Speakman and Stott[3], working with high concentrations of dyes and samples of wool which had been treated with nitrous acid for nearly 100 hours, demonstrated that the affinity of deaminated wool for acid dyes is far less than that of untreated wool. The results they obtained were confirmed by similar experiments in the present investigation, under far less drastic conditions of deamination. A sample of wool yarn was treated with a 10 per cent solution of nitrous acid at room temperature for 3 hours, after which it was washed for 48 hours in distilled water. The treated sample had acid- and acid-dye-combining capacities of 0.5 and 0.4 millimole per gram, respectively.

2. Effect of Hydrogen Peroxide

In an investigation of the effect of hydrogen peroxide on the basic groups in wool[12], it was found that the acid-combining capacity decreased with increased oxidation. The magnitude of these changes was so great as to suggest a similar determination of the acid-dye-combining capacity. Samples of wool were oxidized for different lengths of time with a 3 per cent neutral solution of hydrogen peroxide at 120° F. The effect of the treatment on the basic properties of the wool is shown in Table 3. Both the acid- and the acid-dye-combining capacities decrease at about the same rate with increase in time of oxidation.

TABLE 3

Effect of Oxidizing Wool with 3 Per Cent of Hydrogen Peroxide at 120° F. for Different Lengths of Time on the Acid-and the Acid-Dye-Combining Capacities

Duration of oxidation	*Acid-dye-combining capacity*	*Acid-combining capacity*
hours	*millimole per gram*	*millimole per gram*
0	0.78	0.77
3	.77	.73
7	.68	.60
16	.52	.43
24	.54	.44
43	.34	.33

3. Affinity of Chlorinated Wool for Acid Dyes

Treatment of wool with chlorine or bromine has been claimed by various workers[13] to increase the dye-absorbing capacity of wool. Such claims appear to contradict the well-known ease of oxidation of amino groups by halogens[14] as well as the findings of the present investigation, which show that the acid-combining capacity of wool treated with a sodium hypochlorite solution (containing at pH 8, 8 per cent of active chlorine based on the weight of the wool) decreases from 0.79 to 0.71 millimole. This apparently anomalous behavior of halogenated wool is readily explained by the determination of the rate of ab-

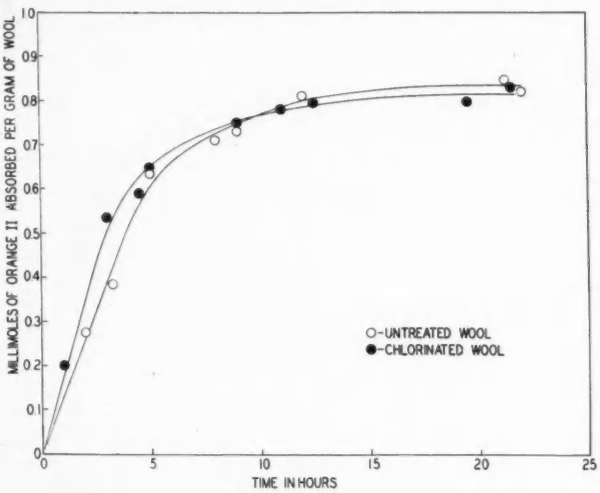

Fig. 1—Comparison of the Rate of Absorption of Orange II by Untreated Wool with That by Wool Which Had Been Treated with a Sodium Hypochlorite Solution Containing 8 Per Cent of Active Chlorine Based on the Weight of Wool.

sorption of acid dye by untreated wool and by wool treated with the sodium hypochlorite solution containing 8 per cent of active chlorine. The curves in Figure 1 show that the initial rate of absorption of dye is much higher for the chlorinated sample, but that at equilibrium slightly more dye is taken up by the untreated sample. The increased rate of absorption of the dye appears to be caused in part by changes in the physical structure of the fiber during chlorination, a factor previously noted by Trotman[16].

4. Nature of the Resist Produced in Wool by the Carbonizing Process

After treatment in the carbonizing process, wool exhibits a decreased affinity for acid dyes and a correspondingly increased affinity for basic dyes. Since a large portion of commercial wool is dyed with acid dyes, this alteration of the affinity of the fiber for dyes is commonly referred to as a resist, although strictly speaking, it is only a resist to acid dyes. The factors which influence the formation of the resist on wool have been pointed out by Ryberg[16].

The present studies on the nature of the acid-dyeing process indicated that the resist was probably formed by decreasing the basic properties of the fiber. However, a mechanism which would account for the decrease in the basicity during carbonizing was not suggested until recently when Harris, Mease, and Rutherford[17] showed that, in addition to a reversible reaction of wool with sulfuric acid, there was a possible irreversible reaction. These are shown in the following equations:

(1.) $RNH_2 + H_2SO_4 \rightleftharpoons RNH_3.HSO_4$

(2.) $RNH_2 + H_2SO_4 \longrightarrow RNHSO_3H + H_2O$

where R represents the portion of the wool to which the basic group is attached.

Equation 1 indicates the reaction which is assumed to take place in dilute solutions of sulfuric acid. The acid in the compound formed in this reaction is reversibly held and is readily replaceable by acid dyes. On the other hand, the reaction represented in equation 2 appears to take place only under dehydrating conditions, for example, in the presence of strong solutions of sulfuric acid. The reaction of basic groups in wool with sulfuric acid, to form sulfamic acid derivatives according to equation 2, not only decreases the basic properties but also increases the acidic properties.

The results of that work immediately suggested that a similar reaction might occur in the carbonizing process, and would not only account for the decreased affinity for acid dyes but also for the increased affinity for basic dyes. Although the concentration of sulfuric acid in the acid-soaking bath seldom exceeds 5 per cent by weight, the acid becomes concentrated on the fiber during the subsequent drying and baking processes and the reaction in equation 2 could occur.

That the formation of the resist is the result of producing a new compound of the sulfamic acid type is demonstrated by the following experiment. Samples of wool cloth were soaked for 15 minutes at 70° F. in solutions of sulfuric acid, varying in concentration up to 20 per cent by weight. The samples were immediately centrifuged to about 40 per cent condition, baked 15 minutes at 250° F., and washed in running distilled water for about a week. The decrease in the acid- and acid-dye-combining capacities and the increase in the alkali-combining capacity[17] and the sulfate content[18] with increasing concentration of acid in the soaking bath are shown in Table 4. Although good agreement between the decrease in acid-combining capacities and the increase in alkali-combining capacities and sulfate content was obtained, the decrease in the acid-dye-combining capacity is low. This discrepancy was accounted for when an examination of the dye baths showed the presence of sulfate. This indicated that hydrolysis of some of the sulfamic acid groups

TABLE 4

Effect of Varying the Concentration of Acid in the Soaking Bath Used in the Carbonizing Process on the Acidic and Basic Properties of Wool

Concentration of H_2SO_4 in the acid soaking bath	*Decrease in acid-dye-combining capacity*	*Decrease in acid-combining capacity*	*Increase in alkali-combining capacity*	*Increase in sulfate content*
Per cent	*Millimole per gram*	*Millimole per gram*	*Millimole per gram*	*Millimole per gram*
4	0.00	0.01	0.04	0.02
8	.01	.13	.11	.09
12	.08	.21	.23	.16
16	.08	.24	.30	.18
20	.11	.26	.34	.28

had occurred during the prolonged dyeing, thus regenerating some basic amino groups.

The data in Table 4 also show that a large proportion of the basic groups in wool are still available for dyeing. Since the number of moles of dye per gram of wool used in commercial dyeings is very much smaller than the residual acid-dye-combining capacities, the visual differences in the color of commercially dyed, carbonized samples indicates that the bulk of the resist is formed on the surface of the fiber. The effect of varying the acid concentration of the soaking bath, as previously described, on dyeings which approximate those obtained commercially is shown in Figure 2. Here, the formation of the resist, as evidenced by the increase in reflectance of the samples dyed with alizarin saphirol, is accompanied by a corresponding increased affinity for basic dyes, as shown by the decrease in reflectance of the samples dyed with crystal violet.

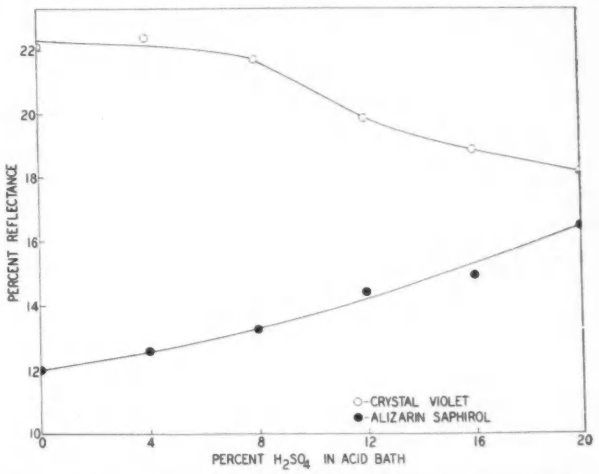

Fig. 2—Effect of Varying the Concentration of the Acid Bath in the Carbonizing Process on the Dyeing Characteristics of Wool Cloth, as Shown by Changes in Reflectance of Light at Wave Length 436 Millimicrons for the Samples Dyed with Crystal Violet, and Wave Length 501 Millimicrons for those dyed with Alizarin Saphirol.

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Joint Rayon Crepe Research

THE American Association of Textile Chemists and Colorists and the Throwsters Institute will report through the pages of the research issues of the AMERICAN DYESTUFF REPORTER, starting with the October 1937 issue, the results of a unique research project. This project is jointly sponsored by the American Association of Textile Chemists and Colorists, Rayon dyers and finishers, Rayon producers, Rayon Throwsters, Rayon weavers and the Textile Foundation.

The research originated with the Throwsters Institute, the immediate inspiration being the pressure of claims involving visible variations in finished fabric that places a heavy burden on all branches of the industries directly or indirectly involved in the manufacture of ladies' Rayon crepe fabrics, whenever the market price of these fabrics declines.

At the request of many of its members the Throwsters Institute took the initiative in seeking for a way of reducing the costly and time consuming claims that periodically beset the entire industry.

Lacking the proper technical advice and lacking sufficient financial resources, and feeling that the related groups should also assist in this work, the Throwsters Institute turned to the American Association of Textile Chemists and Colorists for technical guidance and assistance and to industry, and through the American Association of Textile Chemists and Colorists to the Textile Foundation for financial assistance.

Eventually a plan of action was agreed upon involving the following major points:

1—A Committee, representing the various industries and the American Association of Textile Chemists and Colorists was formed to develop a detailed program and to constantly guide the work during its progress.

2—Financing was arranged by the Throwsters Institute who obtained from industry $2,500 in cash, and the Textile Foundation granted to the American Association of Textile Chemists and Colorists $2,500 for this research.

The membership of the Committee follows:

Member	*Firm*	*Representing*
Dr. H. D. Smith,	A. M. Tenney Associates,	A.A.T.C.C.
Dr. J. Quig,	E. E. du Pont de Nemours & Co.,	A.A.T.C.C.
Dr. F. Bonnet,	The Viscose Company,	A.A.T.C.C.
J. McGibbon,	North American Rayon Co.,	A.A.T.C.C.
V. McCullum,	National Dyeing & Ptg. Co.,	A.A.T.C.C.
Wm. Witte,	National Dyeing & Ptg. Co.,	A.A.T.C.C.
B. L. Hathorne,	Berkeley Products, Inc.,	A.A.T.C.C.
Dr. I. J. Saxl,	E. F. Houghton & Co.,	T.R.I.
H. E. Bishop,	Bliss Silk Throwing Co.,	T.R.I.
C. Epstein,	Liberty Throwing Co.,	T.R.I.
G. Friedlander,	Duplan Silk Corporation,	T.R.I.
E. C. Geier,	Duplan Silk Corporation,	T.R.I.
C. W. Dall,	National Rayon Weavers Assn.,	T.R.I.
G. A. Urlaub,	Throwsters Research Institute,	T.R.I.

The Committee met approximately every ten days for three months drawing up a program, the details of which follow, and obtaining an experienced Research worker satisfactory for this project. Eventually, a detailed program was agreed upon by the Committee and was entrusted to the hands of Mr. W. F. Macia, who was engaged to carry out the Committee's program in detail. The program was divided by the Committee into the following five projects:

1—A survey of twelve throwing plants and four weaving plants to determine the extent of variations found in each individual mechanical process used in the commercial manufacture of Rayon crepe yarns.

2—Determination of the effects of variations of all factors, other than dyeing and finishing, influencing the depth or extent of pebble in crepe fabrics. This necessitated the throwing of 62 lots of crepe filling and the weaving, dyeing and finishing of about 2100 yards of cloth, each lot being handled individually in a commercial manner.

3—Sampling and detailed testing of physical and dyeing characteristics of 2000 skeins of Rayon yarn taken from 1000 cases delivered to plants located in different sections of the country.

4—Determination of effects of variations in the dyeing and finishing operation.

5—Compiling and writing of the report covering the work.

After completing its program and obtaining a Research Fellow to carry out the work, the Committee made the following announcement:

"The object of this entire program is to prove the extent to which variations within each individual phase of the manufacture of finished crepe fabric from the production of the rayon itself through the throwing, weaving and dyeing and finishing operations, manifest themselves as visible variations in finished merchandise.

"It also includes a study of the limitations of each of the various steps in the process; namely, a determination of the variables inherent in processes and equipment today considered normal.

"The final objective of this program is to definitely proved facts which may now be known to some manufacturers; that is, that variations in the rayon processed with the best equipment available and by the best known methods, cannot help but result in minor variations in the fabric. It is the Committee's aim to prove that fabric produced under the best possible conditions will contain certain visible variations in certain constructions, and that such fabric constitutes good delivery."

As the work progressed and as the Committee studied the results obtained, the program was, of necessity, enlarged to some extent as the determination of certain factors made necessary a study of other equally important variables. As finally put into operation, the research followed the outline found at the conclusion of this announcement.

At the end of a year it was found that the initial subscription was insufficient to complete the work and that additional funds would be necessary to carry the work to completion and thus obtain the results originally anticipated. The Committee, through the American Association of Textile Chemists and Colorists, again appealed to the Textile Foundation pointing out that during the progress of the work industry had contributed more than $3,000 in addition to the initial $2,500 in the form of yarn, chemicals, direct labor, etc. The Foundation recognized the direct contributions of the industry and through the American Association of Textile Chemists and Colorists, granted to the research the necessary additional $2,500.

At this time the bulk of the work, with the exception of that involving humidity variations, has been completed. As a substantial part of the data has been compiled into presentable form to date, the Committee finds itself unable to agree on all details.

At the outset the Committee avowed it was their intention to guide the work as intelligently and accurately as possible and, at the conclusion of the work, to publish their joint findings over their joint signatures. As this

involves reconciling the naturally somewhat divers viewpoints of Rayon producers, Rayon throwsters, Rayon weavers and dyers and finishers, it is easy to see that the presenting of the data in a form satisfactory to all cannot help but be a difficult matter.

The American Association of Textile Chemists and Colorists, the Textile Foundation and all other contributors to this research, trust that the work will be speedily concluded and the report published promptly, in order that the maximum amount of good may be obtained by the contributors and by industry at large.

LOUIS A. OLNEY,
Chairman, Research Committee.

Project No. 1

This involved the making of seventy-five hundred direct measurements of tension or strain on the yarn and many other necessary indirect measurements.

A brief summary follows:

Winding Operation

Strain on the yarn—200 tension observations with tension meters
Length of yarn under strain
Hardness or Density of full spools—200 observations with a densiometer
Atmospheric conditions—
Temperature) 5 observations with
Humidity) sling Psychrometer
Linear Running Speed of Yarn (Yards per Minute)—5 observations
Make of Machines
Type of Swifts
Weight of Swifts

Spinning Operation

Strain on the yarn—200 tension observations with tension meters
Length of yarn under strain
Harness or Density of full spools—200 observations with a densiometer
Twist
Make of Machines
Flyer—Type, Make, Weight of wire
Spindle Speeds
Linear Running Speed of Yarn (Yards per Minute)—5 observations
Atmospheric conditions—
Temperature) 5 observations with
Humidity) sling Psychrometer

Redrawing Operation

Strain on the yarn—200 tension observations with tension meters
Length of yarn under strain
Hardness or Density of full spools—200 observations with a densiometer
Make of Machines
Linear Running Speed of Yarn (Yards per Minute)—5 observations

Copping Operation

Strain on the yarn—80 to 200 tension observations with tension meters
Type of Machines
Atmospheric Conditions—
Temperature) 5 observations with
Humidity) sling Psychrometer

Project No. 2

This project carried on in the plants of the Duplan Silk Corporation and the National Dyeing & Printing Co. involved the manufacturing of two thousand yards of cloth, using sixty-two different lots of filling yarn, each being individually processed in a commercial manner under detailed control at all times.

A brief summary of the work covered in this project follows:

(1) *Effects of Variations in the Quantity of Ingredients in the Soaking Baths*

(A) Size and Oil Reduced 30%
(B) Size and Oil Reduced 60%
(C) Size and Oil Increased 30%
(D) Size and Oil Increased 60%

(2) *Effects of Variations in the Gel Strength of the Gelatin in the Soaking Bath*

(A) 200 Gelatin (B) 350 Gelatin
(C) 500 Gelatin

(3) *Effects of Variations in the Quantity of Gelatin and Dextrine in the Filling Size*

(A) No Gelatin, 100% Dextrine
(B) 25% Gelatin, 75% Dextrine
(C) 50% Gelatin, 50% Dextrine
(D) 75% Gelatin, 25% Dextrine
(E) 100% Gelatin, No Dextrine

(4) *Effect of Variations in the Quantity of Oil in the Soaking Bath*

(A) Oil increased 50%
(B) Oil increased 60%
(C) Oil increased 100%
(D) Oil decreased 30%
(E) Oil decreased 60%

(5) *Effects of Variations in the Quantity of Sulfonated Olive Oil and Raw Cocoanut Oil in the Soaking Bath*

(A) 100% Sulfonated, no Raw
(B) 75% Sulfonated, 25%
(C) 50% Sulfonated, 50%
(D) 25% Sulfonated, 75%

(6) *Effects of Variations in the pH of the Soaking Bath*

(A) pH 3.5 (E) pH 7.5
(B) pH 4.5 (F) pH 8.5
(C) pH 5.5 (G) pH 9.5
(D) pH 6.5 (H) pH 10.5

(7) *Effect of Variations in the Skein Extraction, After Soaking*

(A) Extraction Time Increased
(B) Extraction Time Decreased
(C) Quantity of Ingredients in Soaking Bath Increased and Extraction Increased
(D) Quantity of Ingredients in the Soaking Bath Decreased and Extraction Decreased

(8) *Effects of Variations in Skein Drying After Soaking*

(A) Air Dryed
(B) Normal, 150° F. for 3 hours
(C) High Temperature—200° F. for 3 hours

(9) *Effects of Variations During Weaving* 50-60% *R.H.*

(A) Low (B) Normal
(C) High

(10) *Effects of Variations in Twist Setting or Steaming Temperature*

	Dry Bulb	*Wet Bulb*	*Time*
(A)	140° F.	130° F.	3½ hours
(B)	180° F.	175° F.	3½ hours
(C)	180° F.	175° F.	7 hours
(D)	180° F.	175° F.	14 hours
(E)	205° F.	198° F.	3½ hours
(F)	198° F.	182° F.	3½ hours

(11) *Effects of Variations in Warp Size*

(A) Warp Sized Soft (B) Warp Sized Medium
(C) Warp Sized Hard

(12) *Effects of Variations in Cop Steaming Temperature*

	Dry Bulb	*Wet Bulb*	*Time*
(A)	150° F.	140° F.	10 minutes
(B)	150° F.	140° F.	15 minutes
(C)	150° F.	140° F.	30 minutes
(D)	180° F.	175° F.	1 hour
(E)	Not Steamed		

(13) *Effects of Variations in the Tension During Winding at* 50-60% *R.H.*

(A) Low Tension (B) Normal
(C) High Tension

(14) *Effects of Variations in the Tension During Spinning at* 50-60% *R.H.*

(A) Low Tension (B) Normal
(C) High Tension

(15) *Effects of Variations in the Tension During Redrawing at* 50-60% *R.H.*

(A) Low Tension (B) Normal
(C) High Tension

(16) *Effects of Variations in the Tension During Copping at* 50-60% *R.H.*

(A) Low Tension (B) Normal
(C) High Tension

Project No. 3

This part of the program involved sampling of two thousand cases of Rayon, two hundred Denier Viscose process, delivered to commercial plants in different sections of the country.

A brief summary of the work covered in this project follows:

Part (1). Sample at random two thousand cases of raw 200 denier, viscose process yarn delivered to plants in different parts of the country. Remove two skeins from different bundles in each case.

Part (2). Carefully record all case markings, rayon manufacturer, L.N. number denier size, filament number and luster.

Part (3). Open up the skeins and suspend them in a thoroughly conditioned room (70° F. 65% R.H.) for three days, and mark for identification.

Part (4). Divide each skein into three parts by winding the outside on one bobbin, the middle on a second bobbin and the inside on a third bobbin; mark each bobbin so it can be plainly identified with the skein number and the yarn's position on the skein. In winding use Atwood wire swifts each having a uniform width of hub strap and a uniform hub strap weight of six ounces. Run the winder at a speed not exceeding 150 yards per minute.

Part (5). Reel from each bobbin one-half of a sizing skein (225 meters) for denier size tests.

Part (6). Place the bobbin in a conditioning room for two days then make five tenacity and elongation tests on each, spacing the breaks about five yards apart.

Part (7). Take 10 per cent of the total bobbins at random and 5 per cent of the total bobbins of the extreme types as found in the tenacity and elongation tests and make five stress-strain curves on each on a Scott Single Strand Incline Plane tester (Model I-P-2).

Part (8). To determine microscopical variations in the yarn:

(A) Examine microscopically (lateral method) 55 per cent of the skeins once, in the middle portion.
(B) Examine microscopically (lateral method) 15 per cent of the skeins in three places, the outside, middle and inside.
(C) Make cross sections of any abnormal appearing yarns found in A and B and make photomicrographs.

Part (9). Determine dye variations between skeins by knitting yarns from three parts of each skein in regular order outside middle and inside of skein No. 1 and outside middle and inside of skein No. 2, etc., then knit adjacent to one another the extremes as found in all previous tests.

Note: All the work in this project is to be done in a completely controlled atmosphere of 70° F. 65% R.H.

Project No. 4

Project No. 4 involves the dyeing and finishing of approximately one hundred cuts of cloth in each of two different finishing plants. In each instance two full cuts of cloth will be processed, the comparative sampling to be done near the center seam.

A brief summary of the work covered in this project follows:

1—A 2 x 2 fabric embossed with a No. 2 roller.
2—A 2 x 2 fabric embossed with a No. 4 roller.
3—A 2 x 2 fabric not embossed.
4—A 4 x 4 fabric not embossed.
5—A 4 x 4 fabric boiled off on strings.
6—A 4 x 4 fabric boiled off in skein form at the boil.
7—Fabric boiled off in skein form under rising temperature conditions, i.e., set in at 110, given a second bath at 160 and a final treatment at the boil.
8—Fabric run in a continuous machine, normal conditions, set in at the boil.
9—Fabric, continuous boil-off, normal conditions except set in at 180.
10—Fabric, normal continuous boil-off, tension being applied during boil-off.
11—Fabric, continuous boil-off, absolute lack of tension during boil-off.
12—Fabric, normal boil-off, prescoured two hours in soap.
13—Fabric processed without prescouring.
14—Fabric dyed in soap at the boil.
15—Fabric dyed natural or almost so, at the boil.
16—Fabric dried at 300° Fahrenheit.
17—Fabric dried Air-lay dryer run hot as possible.
18—Fabric dried Air-lay dryer very cool and slow.
19, 20, 21, 22—Various drying machines, as used, at natural.
23—Frame 8 per cent warpwise shrink.
24—Frame 11 per cent warpwise shrink.
25—Frame 25 per cent warpwise shrink.
26—Frame 37″ width.
27—Frame 39″ width.
28—Calender heavy.
29—Calender normal.

—♦♦—

A Study of

The Mercerization Process

III. The Effect of Caustic Temperature and Impurities in the Caustic

SIDNEY M. EDELSTEIN*

INTRODUCTION AND SUMMARY

A. The effect of caustic temperature

At the time of discovery of the process of treating cotton cloth with strong caustic soda to obtain increased strength and shrinkage of the cloth, it was recommended that the caustic solution should be used at a temperature of 60 degrees F or lower.[1]

Later, when this process was adapted to the production of luster on cotton yarn and cloth by the application of tension during the caustic treatment, it was again recommended that the caustic solution be kept below 60 degrees F.[2]

In many plants, adherence to this early advice to keep the mercerizing caustic temperature low has necessitated the installation of large and expensive cooling systems.

Most writers on mercerization also have claimed that best results are obtained in mercerization if the temperature of the caustic is kept low.[3, 4, 5, 6, 7] The recommendations of these writers however have been based on the study of only one property of the mercerized material or else on the amount of shrinkage undergone by cotton in the caustic solutions.

Recently, Jennings has stated that many mercerizing plants are doing away with cooling machines and are mercerizing cotton with caustic temperatures ranging from 60 degrees F. to 90 degrees F.[8]

It has been brought out previously that the properties of dye affinity, luster and strength are each important in commercial mercerizations and that thesee properties are not affected in the same manner by variations in the merzerization process.[9] Hence the effect of temperature on mercerization cannot be determined by studying only one of these properties. It was also shown that the amount of shrinkage undergone by cotton in a particular caustic solution is not indicative of the luster, dye affinity or strength that can be obtained by the use of this solution for mercerization.

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The purpose of the present work on the effect of caustic temperature in mercerization has been twofold: first, to determine if better results are obtained at lower caustic temperatures and secondly, what effect caustic temperature variations might have on the properties of the resultant mercerized material.

In this work, skeins of cotton yarn were mercerized in 30 degrees Tw., 35 degrees Tw., 50 degrees Tw. and 65 degrees Tw. at 60 degrees F., 90 degrees F. and 110 degrees F. under a constant tension and the finished mercerized samples were examined for dye affinity, tensile strength, elongation, barium absorption and luster. The force necessary to keep a 30 gm. skein from shrinking in each solution was also determined.

The results are summarized as follows:

1. The lower the temperature of the particular caustic solution, the greater was the tension necessary to prevent the yarn from shrinking in that solution and the greater was the dye affinity and barium activity number of the mercerized yarn.

This effect of temperature was larger in the 30 degrees Tw. and 35 degrees Tw. solutions than in the 50 degrees Tw. and 65 degrees Tw. solutions.

2. The yarn mercerized at 60 degrees F. in all solutions had a slightly higher tensile strength than the yarn mercerized in the corresponding caustic solutions at 90 degrees F. and 110 degrees F. The elongation properties of the mercerized yarn were not affected by the temperature of the caustic.

3. The effect of caustic temperature on the luster of the yarn mercerized in the 30 degrees Tw. and 35 degrees Tw. caustic solutions was large, with the yarn mercerized at the lowest temperature having the highest luster. The luster of the yarn mercerized in the 50 degrees Tw. and 65 degrees Tw. caustic solutions was only slightly affected by the temperature of the caustic solution. The samples mercerized at 90 degrees F. in these stronger solutions showed the highest luster.

B. The effect of caustic impurities

The mercerizing caustic solutions encountered in practice will contain various quantities of sodium carbonate as well as fats and pectic material removed from the cotton being mercerized. The quantities of sodium carbonate may be as high as 4 per cent and the pectic substances may be present to the extent that the caustic solution has acquired a dark brown color.

The quantities of these impurities present in the caustic will depend on many factors such as the amount of exposure of the caustic to the air, the method of recovery of the caustic from the washes and the previous treatment of the cotton material.

Little attention has been paid in the literature to the effect of the presence of these impurities on the mercerizing properties of the caustic solutions.

To determine the effect of these impurities in the caustic on the properties of the mercerized material, skeins of 40/2 cotton yarn were mercerized as above in caustic solutions at 85 degrees F. having a caustic soda content equivalent to 50 degrees Tw. and containing added impurities varying from 0.2 per cent sodium carbonate to 4 per cent sodium carbonate and 1 per cent pectic material.

The results of these experiments showed that the presence of these impurities in the caustic had a detrimental effect on the luster and dye affinity of the final yarn. The greater the amount of impurities in the caustic, the less was the dye affinity and luster of the yarn mercerized in that caustic. The tensile strength, elongation and barium activity number of the mercerized yarn were unaffected by these impurities in the caustic.

PREPARATION OF SAMPLES

30 gm. skeins of 40/2 Mississippi Delta cotton yarn of balanced twist were mercerized in 30 degrees Tw., 35 degrees Tw., 50 degrees Tw. and 65 degrees Tw. caustic solutions containing less than 0.2 per cent sodium carbonate at temperatures of 60 degrees F., 90 degrees F. and 110 degrees F.

Other skeins were mercerized in a 50 degrees Tw. caustic solutions at 85 degrees F. to which solution various quantities of sodium carbonate and commercial pectin were added so that the solution contained successively 0.2 per cent sodium carbonate, 2 per cent sodium carbonate, 4 per cent sodium carbonate and finally 4 per cent sodium carbonate and 1 per cent pectin. The pectin material was boiled with a small amount of caustic solution before being added to the mercerizing solution. This commercial pectin after boiling with caustic was similar in chemical properties to the pectin substance removed from cotton by caustic solutions.

All skeins were held under a tension of 120 lbs. during the caustic treatment and were locked into position during the washing out of the caustic. The machine used for mercerizing and the methods of pre-treating, washing, neutralizing and drying the skeins were the same as previously described.[9,11]. The force required to keep a 30 gm. skein from shrinking in all caustic solutions at the different temperatures was also determined.

The finished samples were examined for dye affinity, tensile strength, elongation, barium absorption and luster.

EXPERIMENTAL RESULTS

A. The effect of caustic temperature

Force to prevent yarn from shrinking

The force required to prevent the yarn from shrinking in a particular caustic solution was greatest when the temperature of that solution was lowest. In the 65 degrees Tw., 50 degrees Tw. and 35 degrees Tw. solutions this force decreased only slightly between 60 degrees F. and 90 degrees F. but dropped rapidly when the temperature was raised to 110 degrees F. In the 30 degrees Tw. solution the decrease in force between 60 degrees F. and 90

TABLE I

Results of the effect of caustic temperature on the properties of the mercerized yarn.

Caustic conc.	*Temp.*	*Force to prevent shrinkage*	*Tensile strength avg. of 4 detms.*	*Elongation in inches avg. of 4 detms.*	*Barium activity number*	*Order of visual grading*	*Luster number*
30° Tw.	60°F.	67.5 lbs.	167 lbs.	2.5 in.	160	1st	2.31
	90°	52.5	165	2.5	142	2nd	2.19
	110°	37.5	150	2.7	131	3rd	1.94
35° Tw.	60°F.	75.0	168	2.5	160	1st	2.30
	90°	67.5	166	2.4	152	2nd	2.24
	110°	52.5	160	2.5	137	3rd	2.14
50° Tw.	60°F.	97.5	180	2.7	162	2nd	2.29
	90°	90.0	170	2.6	162	1st	2.33
	110°	67.5	170	2.7	159	3rd	2.26
65° Tw.	60°F.	102.5	180	2.6	165	2nd	2.28
	90°	97.5	168	2.7	163	1st	2.33
	110°	81.5	170	2.7	160	3rd	2.27

degrees F. was about the same as the decrease between 90 degrees F. and 110 degrees F.

See Table I.

Dye Affinity

Fabrics were knitted from the samples and after being wet out at 140 degrees F. in a 1 per cent sulfonated castor oil solution, were dyed at the boil in a 30:1 dyebath containing 1 per cent direct Brown BT and 20 per cent salt on the weight of the fabrics.

Examination of the dyed fabrics showed that:

1. In all cases, the lower the temperature of the caustic used for mercerizing the samples, the greater were the dye affinities of the mercerized samples.

2. The differences in dye affinity between the samples mercerized at the three different temperatures in the 30 degrees Tw. and 35 degrees Tw. caustic solutions were very great whereas the differences in dye affinity caused by the different temperatures in the 50 degrees Tw. and 65 degrees Tw. were small.

3. For each particular strength of caustic, the difference in dye affinity between samples mercerized at 90 degrees F. and 110 degrees F. was greater than for the samples mercerized at 60 degrees F. and 90 degrees F.

Tensile Strength and Elongation

Four skein break and elongation determinations were made on each sample under standard conditions of temperature and humidity*. An examination of the average values of these determinations which are given in Table I indicate that samples mercerized at 60 degrees F. have slightly higher tensile strength than the corresponding samples mercerized at 90 degrees F. and 110 degrees F. The elongation properties of the samples appeared to be unaffected by the temperature of the caustic used for mercerization.

Barium Activity Numbers[10]

The barium activity numbers of the samples mercerized in the 30 degrees Tw. and 35 degrees Tw. caustic solutions varied greatly with the temperature of the caustic. The activity numbers of the samples mercerized in the 50 degrees Tw. and 65 degrees Tw. solutions were only slightly affected by the temperatures of the solutions. In all solutions however, the lower the temperature, the higher was the activity number of the mercerized sample.

Luster

The samples in the form of small skeins were compared visually for luster and the ratio of the regular reflectance of the sample to the diffuse reflectance of the same sample was determined with a photoelectric instrument. This ratio which is called the luster number is an indication of the luster of the sample. The higher the luster number of the sample, the greater is the luster of the sample as seen visually. The determination of the luster numbers has been used so far only as a check on the visual grading of the samples†.

The results of both determinations showed that there were considerable differences in luster between the samples mercerized at different temperatures in the 30 degrees Tw. and 35 degrees Tw. caustic solutions whereas the differences in luster of the samples mercerized at different temperatures in 50 degrees and 65 degrees Tw. solutions were slight.

The samples mercerized at 60 degrees F. in the 30 degrees Tw. and 35 degrees Tw. caustic solutions showed higher luster than the samples mercerized at the higher temperatures. The luster of the samples mercerized in the 50 degrees Tw. and 65 degrees Tw. caustic solutions at 90 degrees F. was slightly better than the luster of

*These determinations were made by Professor A. H. Grimshaw at North Carolina State College.

†The photoelectric instrument and the determination of luster numbers will be described fully in a future paper.

those samples mercerized at 60 degrees F. and 110 degrees F. Examination of the luster members of the samples also showed that the maximum lusters obtained in each of the caustic solutions were very closely the same.

The order of visual grading and the luster numbers of the samples are shown in Table I.

B. The effect of caustic impurities

The samples mercerized in the 50 degrees Tw. caustic containing added amounts of sodium carbonate and commercial pectin were examined as above. The force required to prevent a 30 gm. skein from shrinking in each solution was also determined.

In addition to the regular visual grading of the samples for luster, small skeins of the yarn mercerized in the caustic containing 0.2 per cent sodium carbonate and of the yarn mercerized in the caustic containing 4 per cent sodium carbonate were given to twenty different men who were inexperienced in comparing the luster of yarns. These persons were each asked to pick the skein having the highest luster.

Force, tensile strength, elongation and barium activity number

The results of the various determinations showed that the presence of amounts of sodium carbonate up to 4 per cent and pectin to the extent of 1 per cent in the caustic had no effect on the force required to prevent the yarn from shrinking in the caustic and on the tensile strengths, elongations and barium activity numbers of the samples mercerized in these caustic solutions. See Table II.

Dye Affinity

Examinations of the fabrics knitted from the samples and dyed with 1 per cent direct Brown BT as above showed that the greater the amount of impurities in the caustic solutions, the less was the dye affinity of the samples mercerized in these solutions. The differences in dye affinity between the samples were small.

Luster

The luster of the samples was also decreased by the presence of sodium carbonate and pectin in the mercerizing caustic. This was shown by visual comparison and by the luster numbers of the samples. (See Table II).

The different persons inexperienced in examining luster were also able to pick consistently the sample mercerized in the 50 degrees Tw. caustic solution containing 0.2 per cent sodium carbonate as having a greater luster than the sample mercerized in the caustic containing 4 per cent soda ash. This indicated that the difference in luster was a practical one.

DISCUSSION

It was pointed out in a previous paper that caustic concentrations near 30 degrees Tw. were very critical in that slight variations in concentration in these solutions could cause considerable variations in the properties of the material mercerized in these solutions[9]. The above work on the effect of temperature also has shown that concentrations near 30 degrees Tw. are critical with respect to temperature. Consequently such concentrations for practical mercerization do not appear suitable.

Commercially, a caustic concentration near 50 degrees Tw. is used for mercerization. The results of the present work and that previously carried out[11] show that the mercerizing power of caustic solutions near 50 degrees Tw. is not very sensitive to variations in concentration and in temperature. We may also conclude that there are no great advantages in cooling a commercial mercerizing solution down to a temperature of 60 degrees F. as is recommended widely in the literature. The dye affinity and strength of the material mercerized at 60 degrees F. in 50 degrees Tw. caustic is only slightly greater than that obtained by mercerization in 50 degrees Tw. caustic at 90 degrees F. The slight increase in these two properties obtained at the lower temperature is more than offset by

TABLE II

Effect of impurities in 50 degrees Tw. caustic on the properties of the mercerized samples.

Impurities	*Specific gravity in degrees Tw. (Westphal balance)*	*Force to prevent yarn from shrinkage*	*Tensile strength avg. of 4 detms.*	*Elongation in inches avg. of 4 detms.*	*Barium activity number*	*Order of visual luster grading*	*Luster number*
0.2% sodium carbonate	50.0° Tw.	90 lbs.	169	2.6	162	1st	231
2% sodium carbonate	51.9° Tw.	90 lbs.	173	2.6	162	2nd	229
4% sodium carbonate	54.2° Tw.	90 lbs.	168	2.6	162	3rd	225
4% sodium carbonate plus 1% pectin	54.8° Tw.	90 lbs.	171	2.6	162	4th	223

the cost of cooling the caustic to 60 degrees F. and by the fact that the luster of the material is slightly inferior to that obtained in a 50 degrees Tw. caustic solution at 90 degrees F. The results of the above work also indicate that it is advantageous to keep the temperature of the mercerizing caustic from varying over a wide range and especially when the temperature is above 90 degrees F. Above 90 degrees F. the properties of the mercerized material change more rapidly with changes in temperature than below 90 degrees F.

The presence of sodium carbonate and pectins decreases the luster and dye affinity of the resultant mercerized material. The higher the amount of impurities, the greater is the decrease in these properties. The presence of impurities in the caustic also gives an apparent specific gravity greater than that due to the caustic alone. This effect may be seen in Table II where the addition of each 1 per cent sodium carbonate to a 50 degree Tw. caustic solution raises the Twaddle of the solution about one degree.

The writer cannot conclude however that only pure caustic solutions should be used for commercial mercerizing. The dye affinity of the mercerized material is only slightly decreased by the presence of several per cent of sodium carbonate and the decrease in luster caused by impurities might be overcome by putting the cotton yarn or cloth under slightly more tension. The factors governing the amount of impurities in the mercerizing caustic differ from one plant to another and the decision as to whether impurities in the caustic of a particular plant can or should be decreased can only be made by the mercerizers within each plant.

It does appear that the amount of impurities in caustic solutions used for mercerization should be kept from varying over a wide range as a wide variation would cause changes in the luster and dye affinity of the mercerized material.

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Variations in the Removal of Pectic Substances from Cotton Yarn in the Mercerization Process as a Source of Dye Affinity Variation in Mercerized Yarn

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INTRODUCTION AND SUMMARY

VARIATIONS in the dye affinity of mercerized yarn are a defect which is still occasionally encountered in practice. These variations in dye affinity are noticeable as alternate dark and light bands ("tiger stripes") in the dyed fabrics knitted from the mercerized yarn.

Previous work of this writer and that of others has shown that variations in the dye affinity of mercerized yarn might occur if there were large variations in the strength of the mercerizing caustic, in the temperature of the caustic, in the amounts of impurities in the caustic or in the amount of tension applied to the yarn during the caustic treatment.[1, 2, 3, 4] Large variations in the drying of yarn after mercerization also have been found to cause variations in the dye affinity of the mercerized yarn.[5]

Little attention has been given to variations in the amount of the non-cellulosic organic constituents removed from cotton yarn in the mercerization process as a cause of dye affinity variation in the final yarn.

This source of dye affinity variation has been studied in the present work and the results indicate that uneven removal of the organic non-cellulosic substances from the cotton during the mercerization process is the most likely cause of "tiger stripes" in the mercerized yarn.

In this work, the conditions under which the organic non-cellulosic constituents are removed from the cotton in mercerization and the effect of their removal on the dye affinity of the final yarn have been studied. Series of

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tests have also been developed which will show whether the dye affinity variation in a particular sample of mercerized yarn is due to an uneven removal of these non-cellulosic substances from the yarn.

The experimental results obtained on 40/2 combed Mississippi Delta cotton yarn are summarized as follows:

(1) Cotton contains besides fats and waxes approximately 2 per cent of organic non-cellulosic material removable by plain water and approximately 3 per cent of additional organic non-cellulosic material removable by 2 to 10° Tw. caustic soda solution (1 per cent to 5 per cent). Variations in the amount of either of these materials removed in any part of the mercerization process cause variations in the direct dye affinity of the final yarn.*

(2) Untreated cotton yarn used in these studies showed no variation in the quantities of these non-cellulosic substances and no variation in dye affinity.

(3) Removal of the fats and waxes from the cotton yarn before or after mercerization has no effect on the direct dye affinity of the mercerized yarn.

(4) In the usual mercerization process, most of the water soluble pectic substances and a small portion of the caustic soluble pectic substances are removed from the yarn. The removal of these substances takes place mostly in the wetting-out baths before the caustic treatment and in the washes following the caustic treatment.

(5) The greater the amount of pectic substances removed from the yarn, the greater is the dye affinity of the final yarn for direct dyes and the less is the affinity for basic dyes. The removal of caustic soluble pectic substances has a much greater effect on the dye affinity of the yarn than the removal of the water soluble pectic substances.

(6) The higher the temperature of the wetting-out baths or caustic washes and the longer the yarn is in these baths, the greater is the amount of pectic substances removed from the yarn being mercerized.

(7) For a definite temperature and time of treatment, the higher the caustic content of the caustic washes (up to 10° Tw.), the greater is the amount of the pectic substances removed from the cotton yarn.

(8) Pressure (squeezing) on the yarn in the wetting-out baths in the mercerizing caustic or in the caustic washes increases the amount of pectic substances removed from the yarn.

(9) If mercerized yarn containing variations in dye affinity due to uneven removal of the pectic material is dyed with Direct Blue RW, the portions containing the least quantity of these pectic materials dye the deepest. On dyeing the yarn with Methylene Blue, the portions of the yarn which contain the least quantities of these substances now dye the lightest. If the yarn is boiled for a sufficient length of time in 10° Tw. caustic, neutralized, washed and dyed again with either dye, the variations in dye affinity are found to have been removed. Mercerized yarns containing dye affinity variations due to any cause other than uneven removal of the pectic substances from the yarn do not act in this manner.

*Since these organic non-cellulosic materials in the cotton are for the most part similar chemically to the class of material called pectins, the term pectic substances is used in this paper to indicate the organic substances aside from fats and waxes that are removable from cotton by water and caustic solutions.

EXPERIMENTAL WORK

I. Non-cellulosic Organic Substances in Cotton

40/2 Mississippi Delta cotton yarn was extracted for several days with benzene and the solvent was evaporated from the extract and the residue was weighed and examined. The residue consisted of fats and waxes and amounted to 0.5 per cent of the weight of the yarn.

The benzene extracted yarn was further extracted with boiling water for several days. The water extract was examined qualitatively and was found to contain a small amount of material which reduced Fehling's solution. On boiling with dilute hydrochloric acid, the extract showed greatly increased reducing powers for Fehling's solution. On treatment with 12 per cent hydrochloric acid a strong test for furfural was obtained. Most of the organic material in the fresh extract could be precipitated with alcohol. The extract also reduced permanganate solution and hydrogen peroxide.

The amount of organic material removed by the water was determined by evaporating a portion of the water extract to dryness, weighing and igniting. This material was found to be about 2 per cent of the weight of the cotton.

The yarn which had been treated with the benzene and water was finally extracted with boiling 10° Tw. caustic (5 per cent) and the extract was examined as above. It was found to contain 3 per cent of an organic material on the weight of the cotton. The extract did not reduce Fehling's solution until boiled with dilute hydrochloric acid. Tests for furfural were also obtained on this extract when boiled with 12 per cent hydrochloric acid. The material in the extract reduced permanganate and peroxide solutions. It was not precipitated by alcohol or by acid.

From the result of these tests and from the fact that these substances extracted from cotton have a mordant action for basic dyes and other materials it would appear that they are related to the class of substances called pectins.

Micro-Kjeldahl determinations on both the water and caustic extracts showed the presence of only a small amount of nitrogenous material.

Examination of the content of pectic substance of commercial mercerized yarns showed that most of the water soluble pectic substances and a small portion of the caustic soluble pectic substances had been removed.

II. Dyeing Tests

Skeins of cotton yarn containing various quantities of the above described pectic substances were prepared by a

series of treatments with boiling water and boiling 10° Tw. caustic and these yarns were finally knit into fabrics and dyed with several direct and basic dyes under a variety of conditions. These dyeings showed that a removal of either type of pectic substance from the cotton caused an increase in dye affinity of the cotton for direct dyes and a decrease in affinity for basic dyes.

It was also determined from these dyeing tests that the differences in dye affinity caused by differences in the quantities of pectic substances in the cotton were most clearly shown by dyeing with Direct Blue RW C.I. or Basic Methylene Blue under the following conditions:

Fabrics made from the yarns are wet-out at 140° F. for five minutes in a 60:1 bath containing 1 per cent of 50 per cent oil on the weight of the water and are then rinsed thoroughly.

The fabrics are then dyed either in a 60:1 dyebath containing 1 per cent Blue RW on the weight of the fabrics at 160° F. for five minutes or in a 60:1 dyebath containing 0.02 per cent Methylene Blue on the weight of fabrics at 120° F. for five minutes. In either dyeing, no salt is added and the fabrics are rinsed in cold water.

These dyeing methods have been used in the experimental work described below.

III. Removal of Non-cellulosic Organic Substances from Unmercerized Cotton Yarn and the Effect on the Dye Affinity of the Yarn

Skeins of 40/2 Mississippi Delta cotton yarn were subjected to the following treatments, knitted into fabrics and dyed with Blue RW and Methylene Blue by the methods described above. The relative amounts of organic material removed were approximately determined by comparing the depth of color of the extracts.

(1) Boiled for various lengths of time from one minute to ten hours in plain water, rinsed and dried.

(2) Boiled for various lengths of time from one minute to ten hours in 1 per cent sulfonated castor oil solution, rinsed and dried.

(3) Wet-out in 1 per cent sulfonated oil at 140° F. for various lengths of time from one minute to two hours, rinsed and dried.

(4) Wet-out for five minutes in 1 per cent sulfonated castor oil solutions at 110° F., 130° F., 160° F. and at boil. Yarn was rinsed and dried.

(5) Boiled in plain water for five minutes or wet in 1 per cent sulfonated castor oil solution five minutes at 140° F. and squeezed during the treatment under different amounts of pressure. Yarn was rinsed and dried.

(6) First extracted with boiling water and then boiled for various lengths of time in 10° Tw. caustic solution. A series was also treated for five minutes in 10° Tw. caustic at 110° F., 130° F., 160° F., 180° F. and at the boil. The skeins were neutralized in dilute acetic acid, rinsed and dried.

(7) Water extracted skeins were boiled for five minutes in 1°, 3°, 6° and 10° Tw. caustic solutions and another series was treated for five minutes in solutions of the same caustic content at 140° F. The skeins were neutralized in dilute acetic acid, washed and dried.

The examination of the water extracts obtained from the above treatments and the fabrics prepared from the yarns and dyed with Blue RW or with Methylene Blue showed that as the time of treatment, the temperature of the water, sulfonated oil solution or caustic solutions were increased, more pectic substances were removed from the cotton yarn and the finished yarn showed a corresponding increase in dye affinity for Blue RW and a decrease for Methylene Blue. After a sufficiently long treatment of the yarn in any of the solutions, no more pectic substances could be detected as being removed from the cotton and there was no further increase in the dye affinity of the yarn for Blue RW or Methylene Blue.

In the caustic treatments, the yarn treated in the strongest solution (up to 10° Tw.) showed the highest loss in pectic substances, the highest affinity for Blue RW and the lowest affinity for Methylene Blue.

If fabrics containing any of the above treated yarns were boiled for a sufficient time in 10° Tw. caustic solution, neutralized, washed and dyed with Blue RW or Methylene Blue, the differences in dye affinity were found to have been removed.

Yarns which were freed of fats and waxes by solvent extraction showed no change in dye affinity for Blue RW or Methylene Blue. Yarns which had been boiled for several days in plain water and then for several days in 10° Tw. caustic, neutralized, washed and dried showed no further change in dye affinity on being wet-out or boiled in water, sulfonated oil solution or in caustic solution. The application of pressure to this yarn in any of these treatments also did not affect the dye affinity of the yarn.

To obtain quantitative data on the relationship between the amount of pectic substances removed from the yarn and the amount of direct dye absorbed by the yarn, a series of skeins were prepared containing various quantities of pectic substance by treatments with boiling water and 5 per cent caustic. The amount of pectic substance removed from each skein was determined by evaporating the extract to dryness, weighing and igniting. The skeins were all dyed together with Blue RW as described above. The amount of dye on each skein was determined by comparing with skeins of yarn dyed to exhaustion with known amounts of Blue RW. The results are given in Table I and graphed in Figure I.

Examination of these results shows that the removal of the caustic soluble pectic substances has a much greater effect on the dye affinity of the yarn than the removal of the water soluble pectic substances. Also there is not much change in dye affinity until the last 20 per cent of the water soluble pectins are removed.

TABLE I

Per Cent Pectic Substances Removed from Yarn	*Per Cent Blue RW Absorbed by Yarn*
0	0.140
1.45 water soluble pectic substances	0.145
1.70 water soluble pectic substances	0.150
1.80 water soluble pectic substances	0.180
2.00 water soluble pectic substances	0.200
3.60 (all of water soluble plus portion of caustic soluble pectin)	0.300
3.90 (all of water soluble plus portion of caustic soluble pectin)	0.320
4.40 (all of water soluble plus portion of caustic soluble pectin)	0.350
4.80 (all of water soluble plus portion of caustic soluble pectin)	0.400
5.00 (all of water soluble plus portion of caustic soluble pectin)	0.500

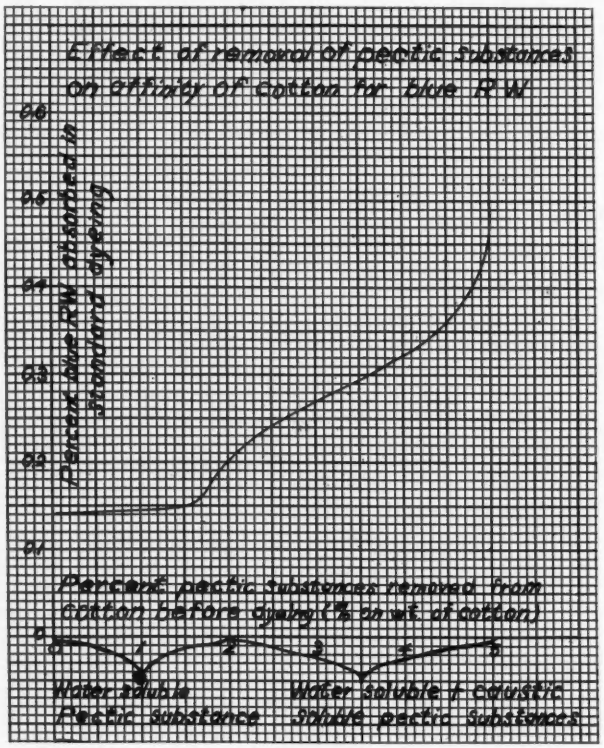
Effect of removal of pectic substances on affinity of cotton for Blue RW
Percent Blue RW absorbed by dyeing
Percent pectic substances removed from cotton before dyeing (% on wt. of cotton)
Water soluble Pectic substance
Water soluble + caustic soluble pectic substances

Fig. 1

IV. Removal of Pectic Substances from the Cotton in the Mercerization Process and the Effect on the Dye Affinity of the Mercerized Yarn

(a) *In the Wetting-out Process*

Skeins of yarn were boiled various lengths of time in plain water, sulfonated oil and caustic solutions, treated for a constant time in different solutions at various temperatures and also squeezed under different pressures during various wetting treatments. These treatments were the same as described in the section above (III) but the skeins were mercerized on an experimental mercerizing machine under a definite tension in 50° Tw. caustic at 80° F. Each skein was washed under tension in 10° Tw. caustic at 140° F., removed from the machine, neutralized in 1 per cent sulfuric acid, rinsed, neutralized in dilute ammonia, washed and dried at 170° F.

The yarns were knitted into fabrics and dyed with Blue RW and Methylene Blue. The same differences in dye affinity were shown by these mercerized yarns which had been wet-out in different manners as were shown by the corresponding unmercerized yarns discussed above (III). Those yarns having the greatest amount of pectic showed the greatest affinity for the Blue RW and the least for Methylene Blue. Fabrics made of these mercerized yarns showed no difference in affinity for Blue RW or Methylene Blue after having been boiled for a sufficiently long time with 10° Tw. caustic.

(b) *In the Caustic Washes*

A set of skeins of 40/2 Mississippi Delta cotton yarn was wet-out at 140° F. for five minutes in 1 per cent sulfonated castor oil solution and another set of skeins were boiled in plain water for thirty minutes. The skeins were mercerized in 50° Tw. caustic at 80° F. for five minutes under a definite tension and a skein from each set was washed under tension in one of the solutions of one of the following washing series:

(1) 10° Tw. caustic at 110° F., 130° F., 170° F. for five minutes.

(2) 10° Tw. caustic at 140° F. for one minute, five minutes, 10 minutes and twenty minutes.

(3) Five minutes at 140° F. in 1° Tw., 3° Tw., 6° Tw., 10° Tw. caustic.

(4) Five minutes at 170° F. in 1° Tw., 3° Td., 6° Tw., 10° Tw. caustic.

(5) In 10° Tw. caustic for five minutes at 140° F. followed by various amounts of pressure on the skein (squeezing) and then continued washing for two minutes in the same solution.

All skeins were neutralized in 1 per cent sulfuric acid, rinsed, neutralized in dilute ammonia, washed and dried at 170° F. The yarns from each washing series were knit into fabrics which were then dyed with either Blue RW or Methylene Blue. Examination of the dyed fabrics showed that the higher the temperature of the washing, the longer the time the yarn was in the washes, the higher the caustic content of the washes (up to 10° Tw.) and the greater the pressure on the yarn during the washing, the greater was the dye affinity of the yarn for Blue RW and the less was the yarn's affinity for Methylene

Blue. Fabrics made from any of the above yarns and boiled for two hours in 10° Tw. caustic, neutralized, washed and dyed with either Blue RW or Methylene Blue showed no differences in dye affinity.

Skeins of cotton yarn were boiled for several days with plain water, then for several days with 10° Tw. caustic, neutralized, washed and dried. These skeins were mercerized in 50° Tw. under constant conditions and washed in different solutions at different temperatures and under different pressures. These yarns were finished. knitted into fabrics and dyed with blue RW or Methylene Blue. No differences in dye affinity were found between these yarns.

(c) *In the Mercerizing Caustic*

Dry skeins were mercerized in caustic containing a penetrant and put under various pressures during the treatment with the strong caustic. The skeins were washed, neutralized and finished under identical conditions. Fabrics made from these yarns and dyed with Blue RW showed that the yarns which had been put under pressure had the highest direct dye affinity. This indicates that variation in the removal of pectic substances can take place in the mercerizing caustic.

(d) *In the Acid Washes and Ammonia Treatment*

Skeins of the 40/2 cotton yarn were wet-out, mercerized, washed and neutralized under identical conditions but were washed at different temperatures up to 160° F. in plain water following the acid treatment. Some skeins were also washed identically following the acid treatment but neutralized in dilute ammonia solutions at different temperatures up to 160° F. Examination of the dyed fabrics prepared from these yarns showed no noticeable difference in dye affinity.

V. Dyeing Properties of Mercerized Yarns Containing Dye Affinity Variations Due to Causes Other Than Variations in Content of Pectic Substances

The results of the above work showed that if there is any variation in the amount of pectic substances removed from cotton yarn during any part of the mercerization process, then those portions of the yarn containing the least quantity of pectic substances will show the greatest affinity for Blue RW and the least for Methylene Blue. Also the difference in dye affinity can be removed by boiling the yarn for a long period in 10° Tw. caustic.

To determine if mercerized yarn having variations in dye affinity due to other causes would act in a similar manner to mercerized yarn having variations in its pectic substance content, a number of fabrics were prepared containing yarns mercerized under widely different tensions, in different strengths of caustic and at different caustic temperatures. Fabrics were also prepared from mercerized yarns containing different amounts of sulfonated olive softener and Glauber salts and from yarns dried at different temperatures after mercerization. The fabrics were dyed with Blue RW and with Methylene Blue and a set of fabrics were also boiled out several hours in 10° Tw. caustic and dyed with Blue RW or Methylene Blue.

In none of these fabrics did the portion showing the greatest affinity for Blue RW show a reversal in affinity for Methylene Blue. Those portions of the yarn dyeing the deepest with Blue RW also dyed the deepest with Methylene Blue. Boiling these fabrics in 10° Tw. caustic before dyeing increased the differences in dye affinity in most cases. No fabric was found which acted in a manner similar to a fabric containing yarn having differences in the content of pectic substances.

DISCUSSION

The above results show that variations in the wetting-out treatment before mercerizing and in the caustic washes, cause variations in the amount of pectic substances removed from the yarn being mercerized and result in the mercerized yarn showing a variation in dye affinity. That these variations in dye affinity are due only to variations in the amount of pectic substances left in the cotton is shown by the fact that if all of the water and caustic soluble substances are removed from the yarn either before or after mercerization, then any variations in the wetting-out treatments or in the caustic washes cause no variation in the dye affinity of the final yarn.

Most of the water soluble pectic substances are easily and quickly removed from the cotton by treatment with plain water and their removal increases the dye affinity much less than the removal of the remainder of the pectic substances. This seems to indicate that this easily removable material is not combined with the cellulose of the cotton.

Since the remaining pectic substances require more vigorous treatment for removal and have a much greater effect on the dye affinity of the cotton, it appears that they are held very strongly by or may be combined chemically with the cotton cellulose.

Variations in the strength, temperature or amount of impurities in the mercerizing caustic, in the amount of tension on the yarn during caustic treatment or in the drying of the yarn after mercerization can cause variation in the dye affinity of the mercerized yarn. These variations must be large, however, in order to cause even a small difference in dye affinity and variations of this type large enough to cause variations in dye affinity are much less likely to be found than the small variations in wetting-out or in the caustic washes which have been shown to cause very noticeable variations in the dye affinity of mercerized yarns.

Finally, it can be shown by the procedure given below whether the dye affinity variations found in any sample of mercerized yarn is due to a variation in the quantities of pectic substances removed from the cotton.

Procedure for determining the presence of a variation in pectic substance content of mercerized yarn:

Three fabrics are knitted from the yarn to be examined.

Two of the fabrics are wet-out at 140° F. for five minutes in a 60:1 sulfonated castor oil bath containing 1 per cent of oil and are then rinsed.

One of the fabrics is dyed in a 60:1 dyebath at 160° F. containing 1 per cent Blue RW on the weight of the fabric for five minutes, rinsed in cold water and dried.

The second fabric is dyed in a 60:1 dyebath at 120° F. containing 0.02 per cent Methylene Blue on the weight of the fabric for five minutes, rinsed in cold water and dried.

No salt is used in either dyeing.

The third fabric is boiled for several hours in two changes of 10° Tw. caustic, neutralized in dilute acetic acid, rinsed thoroughly and then dyed with Blue RW exactly as the first fabric.

If the yarn contains any variation in the amounts of pectic substances, then those portions of the yarn which dyed the deepest with the Blue RW dye the lightest with the Methylene Blue. The fabric which was dyed after boiling in 10° Tw. caustic will show no variation in dye affinity.

Yarn containing variation in dye affinity due to any other cause will not show both the reversal in dye affinity when dyed with methylene blue and the removal of the variations after the boiling in caustic.

Yarn containing noticeable quantities of oxycellulose or hydrocellulose might give positive results for this test but these substances are not likely to be found in yarn which has only been mercerized.

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Luster Determination

with a Photoelectric Photometer

HENRY RANSOM* and SIDNEY M. EDELSTEIN**

INTRODUCTION

SINCE luster is an important characteristic of mercerized material, a quantitative measure of this characteristic has been necessary in the work on mercerization.

Luster is a quality which depends mainly on the light reflecting properties of the material. An examination of the light reflections from certain typical surfaces will help to explain the nature of luster.

In Figure 1 is shown the manner in which a ray of light is reflected from a mirror surface, a matt surface and a semi-matt surface. A mirror surface is one which is smooth, polished and unbroken. A light ray striking this surface is reflected in the same plane and at an equal angle with the surface. A matt surface may be considered to be made of innumerable small mirrors arranged at different angles. Light striking a matt surface is diffused and reflected at many different angles and in several planes. A semi-matt or lustrous surface is typical of mercerized material. This surface acts like a combination of a mirror and a matt surface. A light ray striking a lustrous surface is partly reflected in a regular manner as from a mirror and partly diffused as from a matt surface. The greater the proportion of the light reflected in a regular manner from a lustrous surface, the higher is the quality of luster of that surface.[1, 2, 3, 4]

Fig. 1—Reflection of Light from Different Surfaces.

The eye of a trained observer is able to sum up the various regular and diffuse reflections from surfaces and to obtain a comparison of the luster of the surfaces.

Although an experienced person is able to detect minute differences in luster between samples of mercerized material, he is not able to give a quantitative figure for the luster of a particular sample. Also the eye tires after the comparison of a certain number of samples and the samples become roughened and soiled from handling.

Various types of photometers have been used in the past for obtaining numerical data on the luster of textile materials.[5, 6, 7, 8] Of these instruments the ones making use of a photoelectric cell for measuring the amount of light reflected appear most satisfactory.

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In the present work a photoelectric photometer has been used and has proven very satisfactory for obtaining data on the light reflecting properties of mercerized material.

DESCRIPTION OF PHOTOELECTRIC PHOTOMETER

The instrument consists essentially of an arrangement whereby a sample of yarn or cloth in a fixed position is illuminated at any desired angle with a beam of parallel rays of light from a tungsten filament lamp. The light reflected from the sample at 45 degrees impinges on a photoelectric cell. The voltage generated by the cell is a measure of this reflected light.

The cell used in the instrument is an improved form of the copper oxide photo-voltaic cell and when light is allowed to fall on the cell it generates a current without the application of any external source of voltage.*

The beam of light from the light source is 1½ inch in diameter and the light rays are made parallel by passage through a lens system. This lens system and the light source are fixed to an arm which can be rotated around the sample and fixed at any desired angle.

Since it is difficult to obtain a constant source of light without very large storage batteries or expensive voltage regulators, an arrangement is used in the photometer whereby an ordinary 100 watt bulb on a 120 volt line serves as the light source.

Attached to the light source in a fixed position is a second photo-electric cell which moves with the light source. This second cell is balanced with the cell receiving light from the sample by means of a potentiometer.

It is obvious that if fluctuations in the line voltage change the light striking the sample, then the amount of light reflected from the sample will be changed in the same proportion. Since the measurement made with the instrument is actually a ratio of the light striking the two cells, variation in the light source will have no effect on the results within the limits ordinarily encountered. Figure 2 shows a schematic diagram of the instrument.

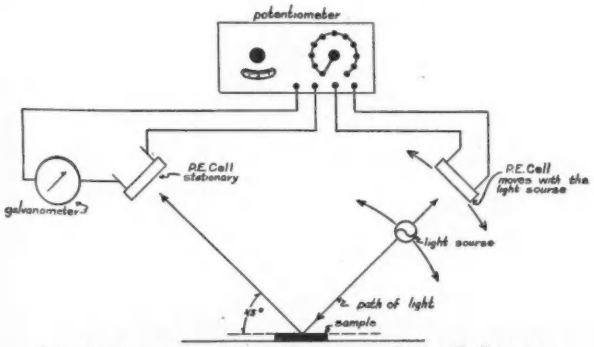

Fig. 2—Arrangement for Measuring Light Reflectance.

*Westinghouse Type SW-30 Photox Cell.

The fabrics are prepared for examination by fixing them evenly on small paper cards. The yarns are wound upon similar cards by a device shown in Figure 3. This device winds the yarn on the card so that all the turns are parallel and next to each other.

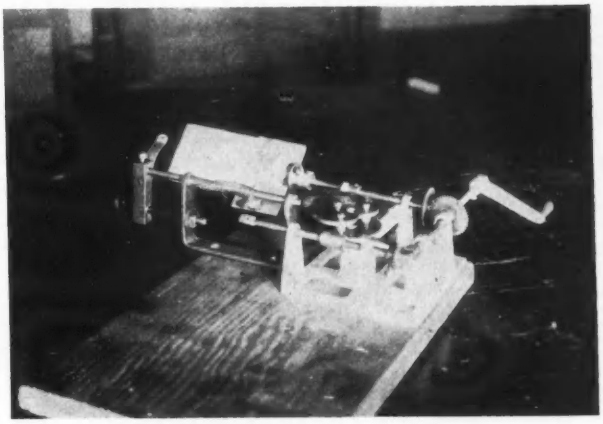

Fig. 3—Device for Winding Yarns.

In making a reading, the card holding the sample is placed in a holder in the machine so that light falls on the sample along the length of the yarn (if fabric, along the warp or filling). The arm on which is fixed the light source is set at the desired angle and then resistances in the potentiometer are put in or out of the circuit until the galvanometer pointer is at zero. The measure of the intensity of the light reflected from the sample is then read on the potentiometer scale. This scale may be standardized against a fixed voltage, a standard sample or it may be used as a fixed arbitrary scale of light intensity.

In the present work a sample of unmercerized cotton yarn has been used as a standard to check the instrument from day to day but the data in the paper are expressed in terms of an arbitrary light intensity scale which has been used throughout.

EXPERIMENTAL WORK

(a) *Yarns*

A large number of various undyed mercerized yarns were examined with the photometer in order to determine what particular set of determinations or figures would give a measure of the relative lusters between samples as seen visually.

In Figure 4 are shown curves of the amount of light reflected by samples of 40/2 combed peeler mercerized yarns when illuminated at different angles. Sample No. 1 was unmercerized, No. 2 was mercerized in 25° Tw. caustic, No. 3 in 40° Tw. caustic and No. 4 in 55° Tw. caustic. Visual grading of these samples showed that No. 2 had considerably more luster than No. 1, No. 3 showed much more luster than No. 2 and No. 4 was only slightly higher than No. 3. Examination of the reflection curves of these samples shows that the sample with the highest luster as

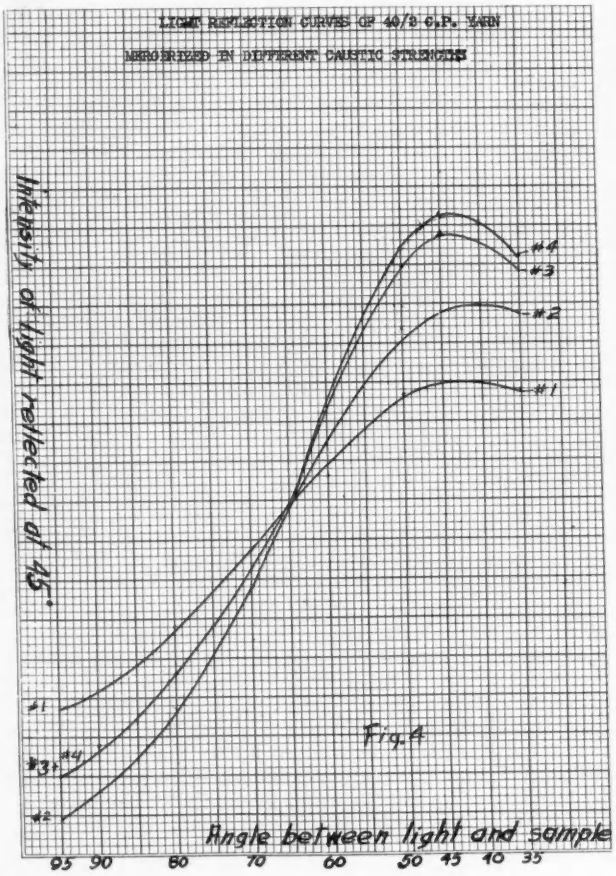
LIGHT REFLECTION CURVES OF 40/2 C.P. YARN
MERCERIZED IN DIFFERENT CAUSTIC STRENGTHS
Intensity of light reflected at 45°
#4
#3
#2
#1
Angle between light and sample
95 90 80 70 60 50 45 40 35

Fig. 4

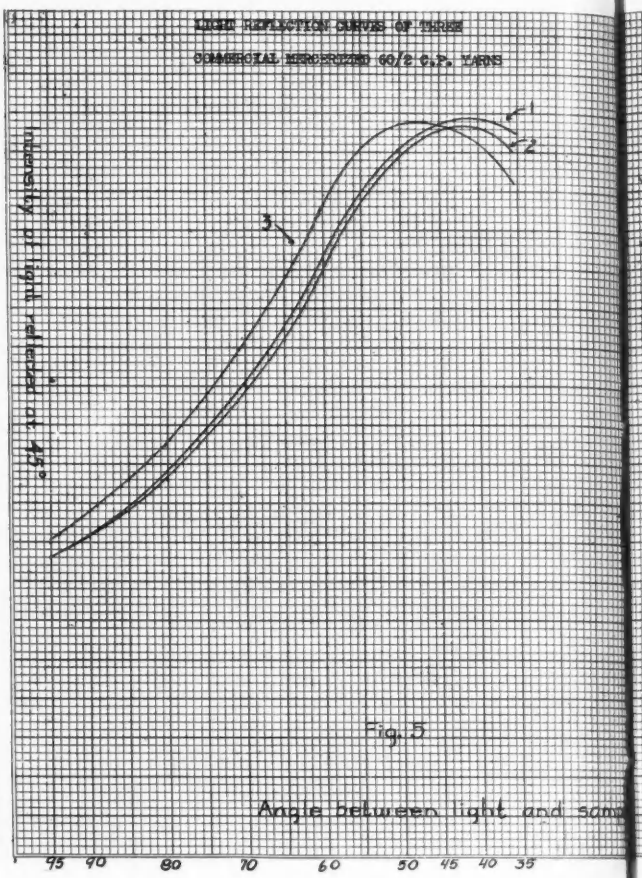
LIGHT REFLECTION CURVES OF THREE
COMMERCIAL MERCERIZED 60/2 C.P. YARNS
Intensity of light reflected at 45°
1
2
3
Angle between light and sam
95 90 80 70 60 50 45 40 35

Fig. 5

determined by visual grading has the highest reflection at 45 degrees and the least at 90 degrees of all the samples.

Since the luster of a surface is due to the excess of light reflected regularly over that reflected diffusely, then if we take the ratio of the light reflected from the sample when illuminated at 45 degrees to that when illuminated at 90 degrees, we obtain a ratio between the regular reflectance and the diffuse reflectance of the sample. These ratios or luster numbers for the above described samples are accordingly: No. 1, 154; No. 2, 189; No. 3, 222; No. 4, 228.

The light reflection curves of three commercial mercerized 60/2 combed peeler yarns are given in Figure 5. Visual luster gradings of these yarns showed that No. 1 and No. 2 were close together, No. 1 being slightly higher than No. 2 and that No. 3 was considerably inferior to No. 2. The luster ratios of these samples are, No. 1, 234; No. 2, 229 and No. 3, 215. It is to be noted that No. 1 and No. 3 show the same amount of reflection when illuminated at 45 degrees and if this figure alone were taken as the basis of luster comparison, then the two samples would be equal. No. 1 and No. 2 have the same amount of reflection when illuminated at 90 degrees and if this figure were also taken alone as the basis of luster comparison, then No. 1 and No. 2 would be the same. From this it is obvious that only a figure which includes both the regular reflectance and the diffuse reflectance of a sample can be used as a measure of the luster of the sample.

While the luster number (ratio of light reflected when illuminated at 45 degrees to that when illuminated at 90 degrees) does not include all of the factors which make up the luster as seen by the eye, it does give a measure of the relative luster of yarns. Thus the higher the luster number of a sample of yarn, the higher is the luster of that sample as seen visually.

A large number of various mercerized yarns have been examined visually for luster and their luster numbers determined as described above. In all cases, the luster numbers have followed the visual gradings.

(b) *Fabrics*

In Figure 6 are shown the light reflection curves for an unmercerized bleached broadcloth and the same broadcloth after mercerization under tension. Measurements were made along the filling and along the warp.

Visual examination of the threads within the mercerized fabric showed that they had acquired a considerable luster yet the reflection curves and luster numbers of the fabric do not adequately show this increase in luster. This is due

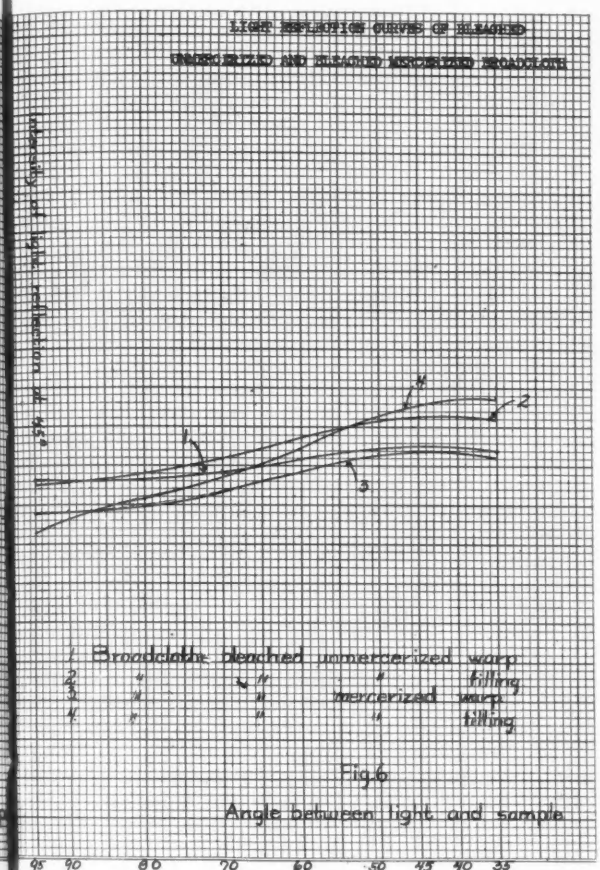
Intensity of light reflected at 45°
1 Broadcloths bleached unmercerized warp
2 " " " filling
3 " " mercerized warp
4 " " filling
Angle between light and sample
95 90 80 70 60 50 45 40 35

Fig. 6

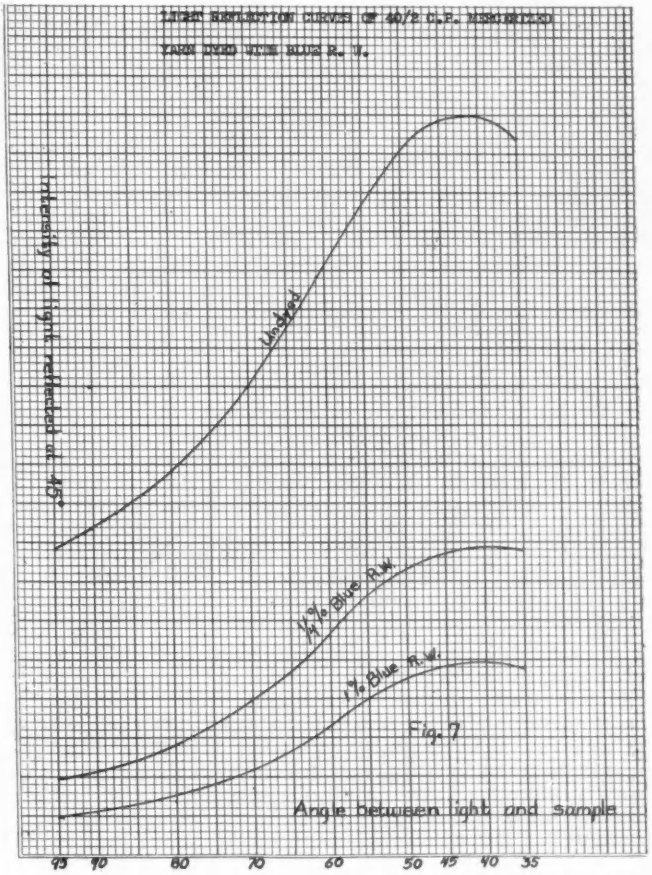

Fig. 7

to the fact that in the photometer, the reflected light that is measured comes from a sample area which includes both warp and filling. Since the warp and filling are at right angles to each other, they tend to cut down the regular reflection and increase the diffuse reflection with a resulting flattening of the reflection curve.

Photometric determinations on this type of fabric obviously cannot be satisfactorily used in luster comparison. Either visual examination must be used with fabrics or else the fabric must be dissected and the warp and filling examined separately with the photometer. The same difficulties were encountered with a large number of various other fabrics.

(c) *The Effect of Color*

Series of samples of the same 40/2 mercerized yarns were dyed with ¼ percent and 1 per cent Blue RW (CI-512) : ¼ per cent and 1 per cent Benzopurpurine (CI-448) and with ¼ per cent and 1 per cent Yellow CH (CI-365). A sample of undyed yarn was also boiled in a salt and sulfonated oil bath, washed and dried under the same conditions as the dyed samples.

The samples in each dye series were compared visually for luster along with the undyed sample and the reflection curve for each sample was determined with the photometer. These curves are shown in Figures 7, 8 and 9.

There was disagreement in the visual gradings of these samples in that to some persons the luster appeared the same whereas to others it appeared that in each dye series, the deeper the shade of the sample the greater was the luster.

Examination of the reflection curves and the luster numbers shows that the addition of dye to the samples decreases the amount of light reflected at all angles but that the diffuse reflection is decreased a greater fraction than the regular reflection. The luster numbers of the samples are given in Table I.

TABLE I
Luster Numbers

	Undyed yarn 229		
Amount of Dye	*Yellow CH*	*Blue RW*	*Benzo-purpurine*
¼%	242	392	355
1 %	252	495	400

The effect of the dye in increasing the luster numbers is explained as follows:

The light which is reflected in a regular manner does not penetrate the surface of the fibers and hence contains considerable white light. The diffusely reflected light,

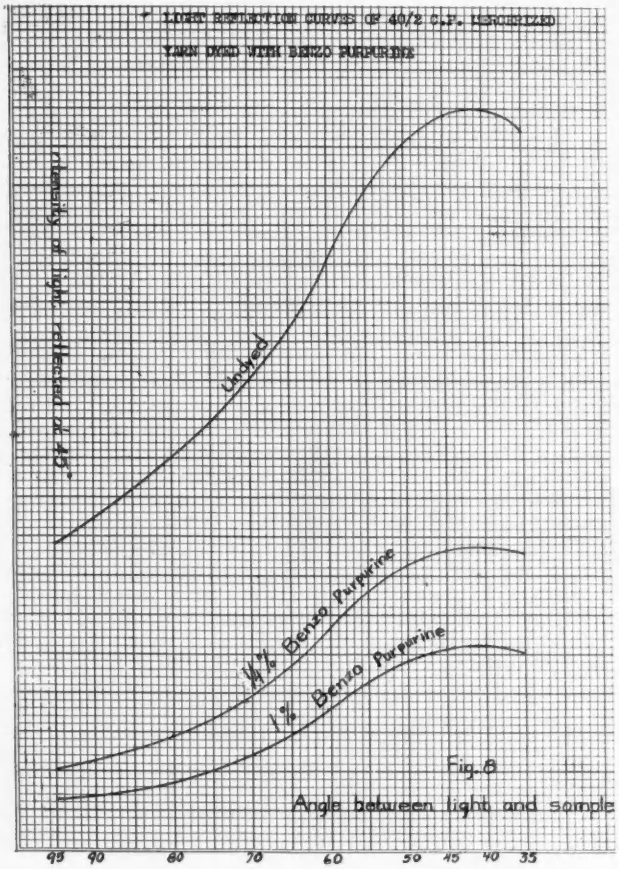
Undyed
1/4% Benzo Purpurine
1% Benzo Purpurine
Intensity of light reflected at 45°
Angle between light and sample
95 90 80 70 60 50 45 40 35

Fig. 8

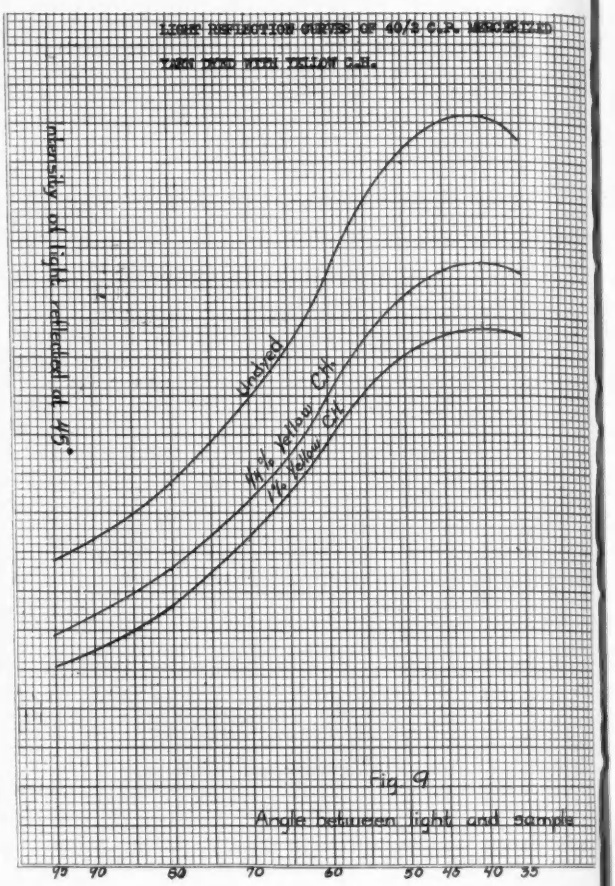

Fig. 9

however, penetrates the surface of the fibers and all of the wave lengths of light are absorbed except those which are characteristic of the dye on the sample. The total light energy of the diffuse light rays is accordingly decreased in a greater proportion than is the light energy of the regular light rays.

The luster of the dyed material is accordingly greater than that of the undyed material when examined in white light. The luster numbers determined photometrically and the visual grading of dyed material include the luster effect due to the structure of the yarn or cloth and the nature of the fibers as well as the effect due to the color, amount and kind of dye on the material.

DISCUSSION AND SUMMARY

The photometer described above has been used to determine the light reflecting properties of a large number of yarns and fabrics. Provided the instrument is standardized before each day's use it gives results which are constant from day to day. The effect of variations in eye sensitivity also does not enter into the determinations as is the case with many other types of photometers.

The arrangement whereby the voltage of the cell receiving light from the sample is balanced against the voltage of the cell receiving light from the lamp has proven valuable for several reasons. First, because the light source can be run on the ordinary light circuit and fluctuations in voltage do not effect the results. Second, the determination of voltage output of the photoelectric cells is a more sensitive measure of the light striking the cell than is the determination of the amount of current. Third, any effect due to the aging of the photoelectric cells will tend to balance out.

A factor which must be considered in light reflection measurements on dyed material is that the human eye is not equally sensitive to all wave lengths of light. In attempting to relate photometric measurements with that which is seen visually, the photometer should have the same sensitivity to the various wave lengths of light as the eye. The photoelectric cells used in the photometer described above have approximately this required sensitivity.

When a comparison of the luster of yarns is desired the determination of the ratio of the amount of light reflected by the sample when illuminated at 45 degrees to that amount reflected by the sample when illuminated at 90 degrees (luster number) is all that is necessary. In the case of fabrics, however, such a ratio does not show the relative luster of the yarns making up the fabric. In examining colored yarn with the instrument the effect of

color in increasing the apparent luster must be realized.

Determination of the complete reflection curves of samples often prove valuable where the factors affecting the luster of the material are being studied.

Acknowledgment

We wish to express our appreciation to Mr. R. S. Hunter and to Mr. W. D. Appel of the National Bureau of Standards for their assistance in this work.

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A Fundamental Study of Vat Printing Pastes

PROJECT 6-33*

II. A Study of the Influence of the Methods of Preparation of Printing Thickeners on the Thickening Value and 'Color Yield'

By SIVERT N. GLARUM†

THE roller printing machine for printing textiles was patented one hundred and fifty-four years ago and has been used since that time with no basic changes. In fact, printing machines well over one hundred years old are still in daily use in some of the most progressive print works. That they are capable of producing a quality and quantity of work comparable to modern machines is indicative of the slight changes that have taken place.

The introduction of the rapid ager about fifty years ago is probably the greatest improvement that has been made in the entire printing process.

Great advances have, however, been made in the dyestuffs used for printing. There are available today complete ranges of colors in numerous classes of dyes. In spite of the many new dyes that have been introduced in the last few years, the vat dyes are generally preferred to all others if the cost is not prohibitive. The colorist prefers to use vat colors, the printer to print them, and as a class they are more permanent than any others. The only disadvantage is the somewhat greater cost. The only way in which the printer may offset this differential in cost is to increase the efficiency of the printing process so that a greater color yield is obtained from the vat dyestuffs that he uses.

It is obvious that such an increase in the color yield is possible since the printers themselves estimate that only one-half of the total amount of dye printed is actually fixed on the cloth.

In order to increase the efficiency of the process a complete understanding of all the operations involved must be had and since only very meager information is available this project was undertaken.

Much of the information that has been obtained is not limited solely to vat colors. The data on starches, gums, and thickeners in general, may be applied to the thickeners used with other classes of colors.

The process of printing vat colors is briefly as follows: The printing color[1] is prepared in the color shop and is composed of the thickeners, such as starches and gums, a reducing agent, usually sodium sulfoxylate formaldehyde, and soda ash or potash. Various other substances such as glycerine are also added but they serve only to assist the action of the other materials. On the printing machine this color is furnished to an engraved copper roller, the excess being removed by a doctor blade, and transferred to the cloth which is then passed over drying cans. The printed cloth is passed through an ager and then through an oxidizing bath to fix the dye on the fibers. These are the operations in which the dye is directly concerned and which must be studied in detail.

In a previous paper[2] it was shown that certain physical properties are required in a printing color and methods of measurement were described. If the properties of the

*This project is being carried out by the Research Committee of the A.A.T.C.C., the Sub-Committee on Textile Printing Pastes acting as advisors. This Sub-Committee is composed of Wm. H. Cady, Chairman, Arthur E. Hirst, Morell Mackenzie, Louis A. Olney, Robert E. Rose and Earle K. Strachan. The project has been made possible through an allocation from the Textile Foundation.

†Research Associate of the A.A.T.C.C. Through the courtesy of Brown University, the facilities of the Jesse Metcalf Chemical Laboratory have been available for this work.

[1]The terms "color" and "printing color" are used in this report to designate the paste containing the dyestuff, chemicals, and thickeners, which is usually used in printing machine.

[2]Am. Dyestuff Reptr., *25*, 150 (1936).

printing color fall within certain specified limits, that color will always give a good print as far as its mechanical properties are concerned. No attempt was made to show any relation with the "color yield."

The study of printing pastes is at present progressing along three separate lines which will be coordinated as they are developed. Each has a very direct bearing on the subject but they are quite distinct at their present stages. It is, therefore, most convenient to take up each of these lines of investigation separately.

I. THICKENERS

The physical requirements of printing thickeners and methods of measurement have been described in previous papers.[2, 3, 4, 5] It has been proven that the printing qualities of a color may be foretold from the measurement of its properties in the laboratory by means of the Stormer viscometer. Definite limits have been established for the flowing properties of colors that will produce good prints on specific types of work.

The next requirement is to determine how to produce printing colors possessing these desired properties.

The factor of "color yield" was purposely omitted from previous studies to simplify the attack on the problem. The importance of this factor was not however overlooked. A study of the relation of "color yield" to the properties of thickeners has therefore been made simultaneously with a study of the methods of preparation of printing thickeners.

There is no readily available method for determining the "color yield" other than by a visual comparison of the prints and many factors serve to complicate such a comparison. The thickener, the engraving, the roller pressure, the ageing, the oxidation, etc., all influence the "color yield." The effect of any one of these factors can be determined only by keeping all other factors constant throughout the test. This can best be done by making comparisons of the colors that have been printed on a single patch of cloth, as it is only in such a case that factors of pressure, ageing, oxidation, etc., may be assumed to be nearly constant.

The entire problem was attacked empirically. The thickeners were prepared, their flow curves measured, printing colors prepared and printed, and the prints compared. Each experiment had to be repeated many times with consistent results before any conclusions could be reached. It is obvious that such a study requires the preparation and testing of thousands of samples before an accurate understanding of the behavior and action of these materials is attained.

A. *Method of Preparation.*

The method of preparing a thickener has a great influence on its properties. Small variations in temperature, stirring, etc. have relatively large effects on the properties of the thickener produced. The apparatus used for heating and stirring the samples of thickeners is shown in Figures 1 and 2. It has proved most valuable in the present study.

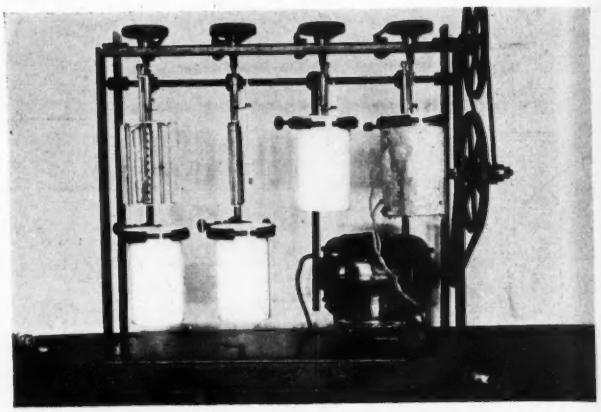
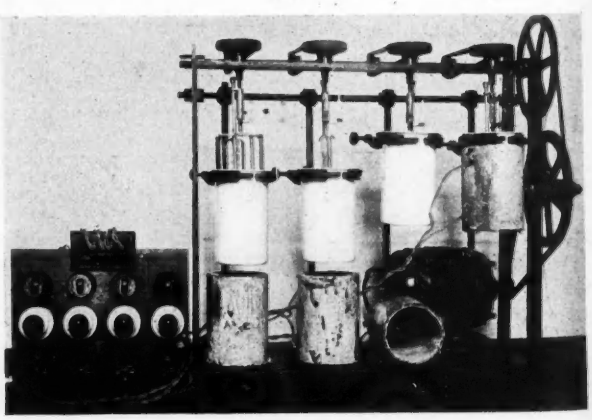


Fig. 1—Stirring apparatus used for preparing thickeners.

The stirring apparatus is constructed so that four samples may be prepared at one time. The stirrers are driven from a single shaft at a speed of twenty-four revolutions per minute. The variation in speed is less than one revolution per minute. Due to the thickness of the materials to be prepared, the ordinary types of stirrers are inadequate. After many trials, stirrers were constructed that have two vanes which are held against the walls of the cooking vessel by a slight tension and serve to prevent any paste from adhering to the walls during cooking. In order to prevent the mass of paste in the center of the vessel from revolving with the stirrer without any agitation, a second stirring member was inserted. This is geared to the large stirrer but revolves about its own axis which is off center from the axis of the main stirrer. This arrangement gives a thorough mixing and produces a uniform temperature throughout the paste. Brackets are

Fig. 2—Complete stirring apparatus with heater and control panel.



[2]Am. Dyestuff Reptr., *23*, 175 (1934).
[4]ibid., *26*, 33 (1937).
[5]ibid., *26*, 124 (1937).

also provided for a thermometer so that the temperature may be read at any time. The general arrangement is shown in Figure 1. The complete apparatus with heater and control panel is shown in Figure 2.

Porcelain beakers, size 4, are used as cooking vessels and heat is supplied by electric heaters which were constructed to fit tightly around the walls of the beakers. These heaters, about 200 watts each, were made as nearly alike as possible and showed practically identical heating curves during trial runs. All heat is supplied through the side walls of the beakers and the temperature is controlled by means of resistances in series with the heaters. Very satisfactory results have been obtained with this arrangement. Thickeners may be prepared at any temperature up to their boiling point.

B. *Determination of Flow Curves.*

The method used for determining the flow curves of printing colors has been described in detail in a previous article.[2] The high density of these thickeners required the use of 110 gram samples instead of the 100 gram samples used previously, but otherwise the procedure remained unchanged.

C. *Standard Formula.*

It was necessary to choose some formula for a thickener which could be taken as a standard. The knowledge of how various factors affect this thickener may then be applied to other thickeners after checking to see if they have same general behavior. The following formula was selected as an average of those used in several print works for cotton printing.

Standard Thickener Formula

6 %	Starch
6 %	British Gum (80% soluble corn)
13½%	Soda Ash
12 %	Sulfoxylate
6 %	Glycerine
56½%	Water
100 %	

Various assistants such as mineral oil, turpentine, stearic acid, etc. have been omitted to simplify the tests. Corn, wheat, and tapioca starches have been studied in this basic formula.

D. *Experimental Results.*

The effects of each of the following factors on the properties of thickeners made from this basic formula have been studied.

1. Length of cooking.
2. Temperature of cooking.
3. Dilution after cooking.
4. Addition of alkali at various stages of cooking.
5. Effect of dyestuff on printing thickener.

1. *Length of Cooking.* There is a great deal of variation in the length of time that thickeners are cooked in various color shops. There is even a considerable variation within a single color shop. If there is any uniformity in the methods of preparation it is that the thickeners are almost universally insufficiently cooked.

The stirrers in plant kettles are very inefficient and allow a thick layer of starch or gum to adhere to the walls of the vessel. This quite effectively insulates the remainder of the paste from the source of heat. It is seldom that an average temperature of 190° F. is attained. The length of cooking under these conditions may vary from one-half to two hours including the time required to heat the material.

It is probable that the majority of the troubles encountered in printing colors may be traced directly to improper preparation of the thickeners. However, little attention is given this operation until trouble is encountered. There are almost no data available on the proper methods of preparing these thickeners so that maximum thickening value and "color yield" may be obtained.

Procedure. The cooking was started with the starch, British Gum and water in the cooking beakers. When the starch had thickened (about 175° F. with corn starch), the soda ash was added and the cooking continued for the specified time at a temperature of 205° F. to 210° F. Boiling water was added every one-half hour to replace that which evaporated so that there were only slight changes in concentration during the preparation. At the end of the cooking time, the heaters were removed. Stirring was continued until the samples were cooled to room temperature, the sulfoxylate and glycerine being added at about 150° F.

The pastes were allowed to stand overnight, then strained and the flow curves measured. Each sample was then divided into three portions and 10 per cent printing colors were prepared using Ciba Blue 2BD, Ponsol Jade Green Supra, and Calcoloid Pink FF. This gave a series of printing colors containing each of the dyestuffs and these colors were printed on a single patch of cloth. Since three dyestuffs were used, three prints were made for each series of thickeners. These prints were aged in plant agers, oxidized, and then the printing colors on each of the patches of cloth were compared for "color yield".

Corn Starch. Thickeners were prepared according to the standard formula using corn starch. Samples were cooked for ½, 1, 2, 3, and 4 hours and then tested as described above.

Space does not permit showing the results of all the experiments that have been made but the flow curves for a typical series are shown in Figure 3.

These curves show very conclusively that *the longer the period of cooking the greater the thickening value.* Many other trials have without exception confirmed this conclusion. This does not agree with the opinions held in many color shops, but it does agree with some of the more modern theories of starch behavior.

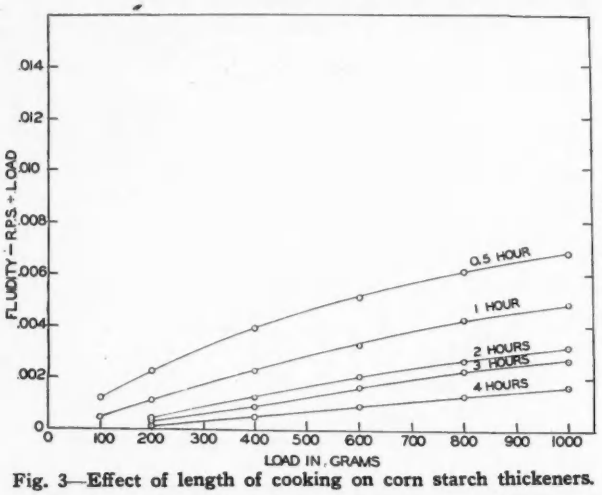


Fig. 3—Effect of length of cooking on corn starch thickeners.

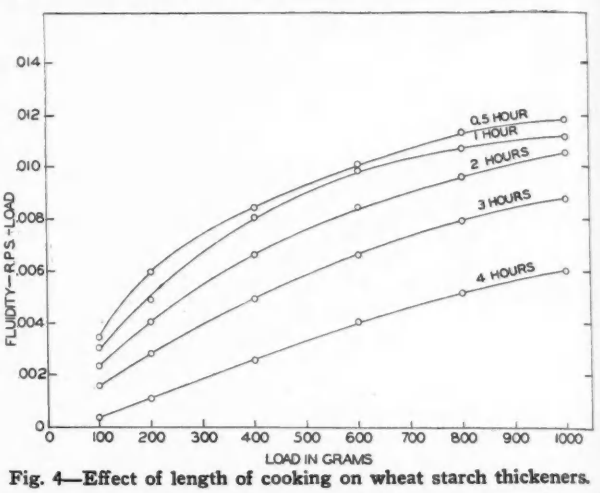


Fig. 4—Effect of length of cooking on wheat starch thickeners.

Table I. Effect of length of cooking on "color yield" of corn starch thickeners.

Hours cooked	*Exp.* 121 Order of "color yield"			*Exp.* 123 Order of "color yield"			*Exp.* 125 Order of "color yield"		
	Pink	*Blue*	*Green*	*Pink*	*Blue*	*Green*	*Pink*	*Blue*	*Green*
½	1	1	1	1	1	1	1	1	1
1	2	2	2	2	2	2	2	2	2
2	3	3	3	3	3	3	3	3	3
3	4	4	4	4	4	4	4	4	4
4	5	5	5	5	5	5	5	5	5

Colors made from these thickeners were printed and the "color yields" were compared. The results from several series of thickeners are shown in Table I.

The first column shows the length of time the thickener was cooked at a temperature of 205° F. to 210° F. Across the top is given the experiment number of the series of thickeners from which the data were obtained.

The words "pink", "blue" and "green" at the head of the columns refer to the dyestuff used and these have been described above. The numbers in the columns indicate the order of "color yields" of the thickeners with each dyestuff. The higher the number the greater the "color yield". For example, under Exp. 121, Pink, are given the gradings of "color yield" of printing colors made with Calcoloid Pink FF from the series of thickeners produced in Experiment 121. The poorest "color yield", indicated by the number 1, was given by the color made with the thickener that was cooked one-half hour. The next best "color yield", indicated by number 2, was produced with the thickener cooked for one hour. The number 5 indicates the maximum "color yield" of the series which was produced by the thickener that was cooked for four hours.

These data show that with corn starch *there is a very definite increase in "color yield" as the time of cooking of the thickener is increased.*

Wheat Starch. Wheat starch thickeners were prepared according to the standard formula and cooked for ½, 1, 2, 3, and 4 hours. A typical series of flow curves is shown in Figure 4. The longer cooking produces thicker pastes the same as with corn starch.

The results of the tests for "color yield" are shown in Table II.

Table II. Effect of length of cooking on the "color yield" of wheat starch thickeners.

Hours cooked	*Exp.* 133 Order of "color yield"			*Exp.* 134 Order of "color yield"		
	Pink	*Blue*	*Green*	*Pink*	*Blue*	*Green*
½	2	2	1	1	2	2
1	1	1	2	2	1	3
2	3	3	4	3	3	1
3	4	5	3	4	5	4
4	5	4	5	5	4	5

These results do not fall in the exact order as did the results with corn starch but, nevertheless, they show that there is a definite increase in "color yield" as the length of cooking is increased which agrees with the results of the tests with corn starch.

2. *Temperature of cooking.* Samples of thickeners were prepared according to the standard formula and cooked for two hours at 180°, 190°, 200°, and 210°. The flow curves and "color yields" were determined as before.

Corn Starch. Typical flow curves of corn starch thickeners prepared at different temperatures are shown in Figure 5.

These curves show that the higher the temperature at which the pastes are cooked the greater is the thickening value.

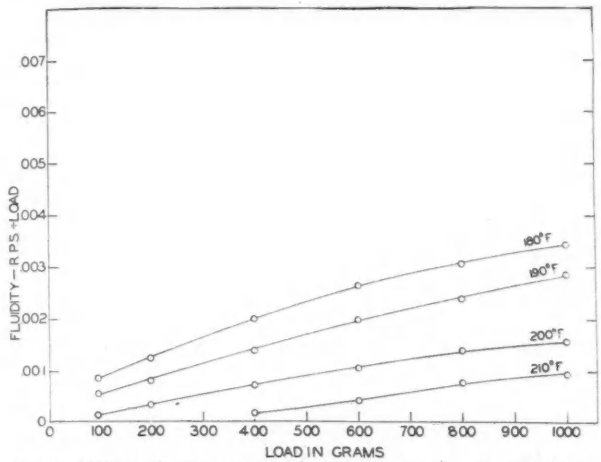


Fig. 5—Effect of temperature of cooking on corn starch thickeners.

Table III. Effect of cooking temperature on "color yield" of corn starch thickeners.

Temp. of cooking	*Exp.* 422 *Order of "color yield"* Pink	Blue	Green	*Exp.* 426 *Order of "color yield"* Pink	Blue	Green
180°	1	1	1	1	1	1
190°	2	2	2	2	2	2
200°	3	3	3	3	3	3
210°	4	4	4	4	4	4

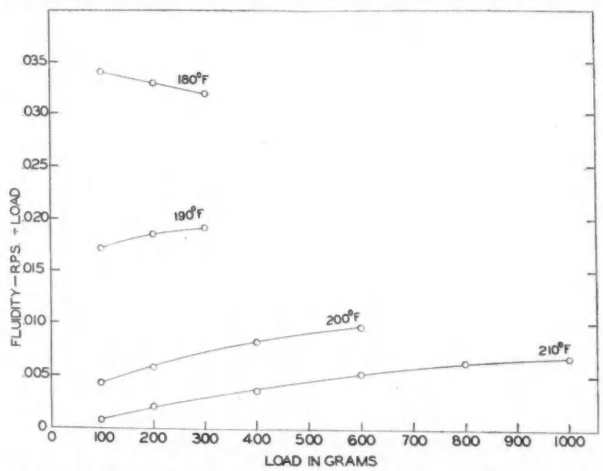


Fig. 6—Effect of temperature of cooking on wheat starch thickeners.

Table III shows the effect of cooking temperature on the "color yield".

It is apparent from these data that *the "color yield" and thickening value of corn starch thickeners are increased as the temperature of cooking is increased.*

Wheat Starch. Typical flow curves of wheat starch thickeners cooked at different temperatures are shown in Figure 6.

These, like corn starch pastes, show an increase in thickening value when prepared at higher temperatures. The loss in thickening value of the wheat starch pastes prepared at the lower temperatures is, however, enormously greater than in the case of corn starch. The samples prepared at temperatures below 200° F. are so thin that they can hardly be considered as printing thickeners.

Table IV. Effect of cooking temperature on "color yield" of wheat starch thickeners.

Temp. of cooking	*Exp.* 431 *Order of "color yield"* Pink	Blue	Green	*Exp.* 433 *Order of "color yield"* Pink	Blue	Green
180°	1	2	1	1	1	1
190°	3	1	3	2	2	2
200°	2	3	2	3	3	3
210°	4	4	4	4	4	4

Table IV shows the relation of cooking temperature to the "color yield".

These data also show that the "color yield" is increased as the temperature of cooking of the wheat starch thickener is increased.

Tapioca Starch. Similar experiments were carried out using tapioca starch and cooking at different temperatures. The temperature effect on these thickeners was so slight that the flow curves and "color yields" showed no significant differences.

3. *Dilution after cooking.* It is the practice in many color shops to cook up a thickener at about two thirds of its final volume and add the remainder of the water at the end of the cooking period to cool it down more rapidly. Tests have shown this practice to be very detrimental to the production of good thickeners.

Corn Starch. Corn starch thickeners were prepared according to the procedure described under length of cooking. All were cooked for one hour. The amounts of starch and British gum were varied from that given in the standard formula but the concentrations of all the other ingredients were kept constant throughout.

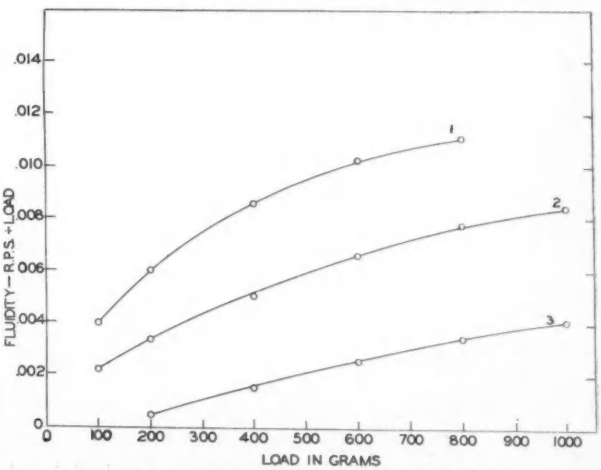


Fig. 7—Effect of dilution on corn starch thickeners.

No. 1 was prepared using 10 per cent Starch and 10 per cent British Gum.

No. 2 was prepared using 8 per cent Starch and 8 per cent British Gum.

No. 3 was prepared using 6 per cent Starch and 6 per cent British Gum.

No. 4 was prepared using 4 per cent Starch and 4 per cent British Gum.

These were then diluted with a solution of the other ingredients to make all samples contain 6 per cent starch and British Gum. The 4 per cent sample was discarded as it was too thin. The flow curves are shown in Figure 7.

Each of the samples whose flow curves are shown here contains exactly the same materials in the same amounts. The curves show clearly the enormous loss in thickening value of pastes when they are diluted after cooking.

Table V shows the effect of dilution on the "color yield" of corn starch thickeners.

Table V. Effect of dilution on "color yield" of corn starch thickeners.

Conc. of cooking	*Order of "color yield"*			*Order of "color yield"*		
	Pink	*Blue*	*Green*	*Pink*	*Blue*	*Green*
10%	1	1	1	1	1	1
8%	2	2	2	2	2	2
6%	3	3	3	3	3	3

These results show definitely that the "color yield" is decreased if the thickener is cooked at a higher concentration than desired and then diluted after cooking.

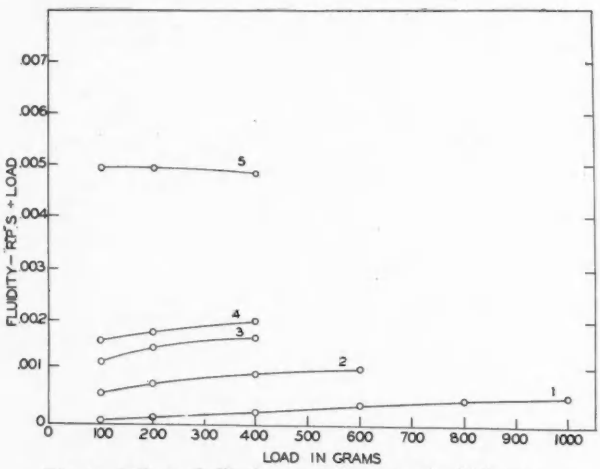


Fig. 8—Effect of dilution on wheat starch thickeners.

Wheat Starch. Tests on the effect of dilution on wheat starch thickeners gave results similar to those obtained with corn starch.

In preparing these samples the following amounts of water were deducted from the amount required by the standard formula and added after the cooking was completed. The final weight of each sample was 600 grams.

No. 1. Standard formula prepared by standard method.

No. 2. 50 grams of water was omitted until end of cooking.

No. 3. 75 grams of water was omitted until end of

No. 4. 100 grams of water was omitted until end of cooking.

No. 5. 150 grams of water was omitted until end of cooking.

The flow curves of these samples are shown in Figure 8.

The "color yields" of these samples followed exactly in the order of dilution, sample No. 1, which was not diluted, giving the maximum color yield.

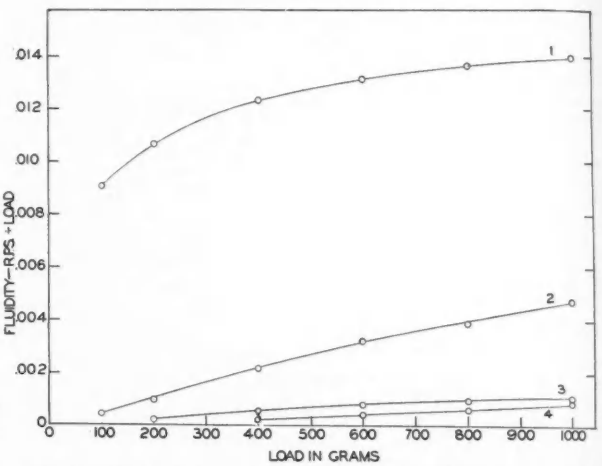


Fig. 9—Effect of time of addition of soda ash on corn starch thickeners.

These results show that maximum thickening value and "color yields" are obtained in the case of wheat starch thickeners if they are not diluted after the cooking is completed.

4. *Addition of alkali at various stages of cooking.* This is another factor in which there is a great deal of variation between plants. Many printers recommend cooking the soda ash in with the starch while others do not add it until the cooking is completed.

Thickeners were prepared following the same procedure as described except that they were all cooked for one hour and the soda ash was added at different stages.

Corn Starch. Typical flow curves of corn starch thickeners to which the soda ash was added at different stages of cooking, are shown in Figure 9.

Thickener No. 1. The soda ash was added before starting to heat.

Thickener No. 2. The soda ash was added as soon as starch was well thickened. (About 175° F.)

Thickener No. 3. The soda ash was added at end of cooking period, before cooling.

Thickener No. 4. The soda ash was added after cooking and cooling to room temperature.

These results show that the less the soda ash is permitted to act on the starch, the greater the thickening value.

Table VI shows the effect of adding the alkali at various stages on the "color yield" of the pastes.

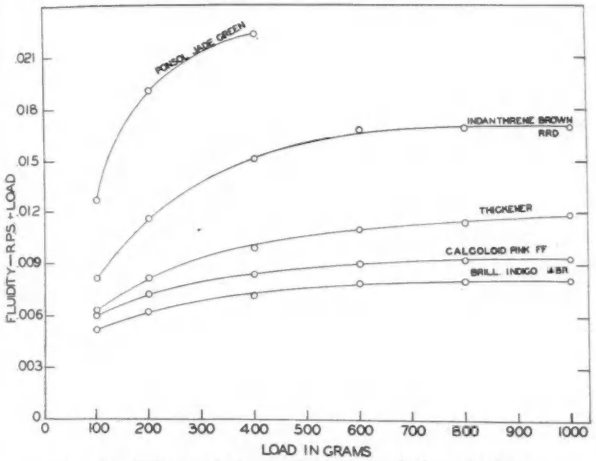


Fig. 10—Effect of dyestuffs on a printing thickener.

Table VI. Effect of time of addition of alkali on "color yield" of corn starch thickeners.

	Exp. 323 Order of "color yield"			*Exp. 324* Order of "color yield"		
Sample	*Pink*	*Blue*	*Green*	*Pink*	*Blue*	*Green*
No. 1	1	1	3	2	1	1
No. 2	2	2	1	1	2	2
No. 3	3	3	2	3	3	3
No. 4	4	4	4	4	4	4

These data show that the less the thickener is acted upon by the soda ash the greater is the "color yield."

These conclusions agree with the practice in many print works of adding the alkali when cooking is finished. Practically it would be difficult to insure complete solution if it were added after cooling.

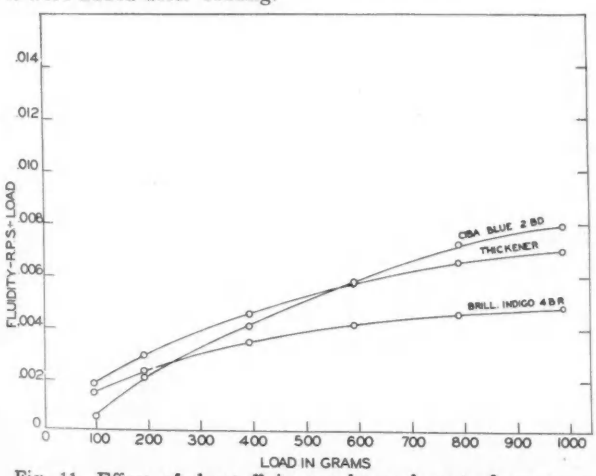


Fig. 11—**Effect of dyestuff in powder and paste form on a printing thickener.**

5. *Effect of dyestuff on the printing thickeners.* One question that is frequently asked is "What effect does the dyestuff have on the properties of the printing color?" Figure 10 shows the enormous variations in the flow curves of printing colors containing various dyestuffs.

Each of these printing colors contained 20 per cent of dyestuff except E, which contained 10 per cent of a double strength dyestuff. All were prepared with a single thickener whose flow curve is shown as A.

A—Original thickener.
B—20 per cent Brilliant Indigo 4BR powder.
C—20 per cent Ponsol Jade Green Supra.
D—10 per cent Calcoloid Pink FF Double.
E—20 per cent Indanthrene Brown RRD.

The results show the great need for control methods in the preparation of standard colors in the color shop.

Figure 11 shows an interesting comparison of the flow curves of colors made with different forms of the same dye.

The Brilliant Indigo 4BR powder gives a color which is somewhat thicker but which has the same shape of flow curve as the original thickener. The same concentration of Ciba Blue 2BD produces a different shape of curve. With this dyestuff the printing color is thinner at the high end of the flow curve than the original thickener but at the same time is thicker at the low stress end. This shows that the printing colors produced have quite different properties.

6. *The effect of various starches.* The effect of substituting various other starches for corn starch in the above formula has been studied. Thickeners were made with tapioca, corn, wheat, potato, and rice starches. Four 20 per cent and four 5 per cent colors were made with each of these using the following dyestuffs:

1. Brilliant Indigo 4BR.
2. Algol Scarlet GGNA.
3. Ponsol Jade Green Supra.
4. Indanthrene Brown RRD.

These were printed and the prints compared for "color yield." The colors prepared with thickeners made from rice and tapioca starches showed outstanding "color yields" compared to the others.

Difficulty has been encountered in practice in using tapioca starch in thickeners but our study of this starch shows that it can be made to produce a very satisfactory thickener if properly cooked.

E. *Conclusions*:

This study has shown that the method of preparation of printing thickeners has a great influence on the thickening power and "color yield" of the thickener. These experiments have shown that the greatest thickening power and "color yield" is obtained from both corn and wheat starch thickeners when:

1. Cooked for a long period of time.
2. Cooked at a high temperature.

3. Cooked at the desired concentration and not diluted after the cooking.
4. The alkali is added at as late a stage of the preparation as is practical.

The data on the effects of dyestuffs on the thickener in preparing color standards show the imperative need for control methods if color standards with uniform properties are to be produced.

II. "COLOR YIELD"

The usual method of determining the "color yield" of a printing color is to make a visual comparison of prints made with that color and another color that is taken as a standard. This so-called standard is itself not a definite quantity but will show variations from one print to another. At best it can only be said that one color gives a better or poorer "color yield" than the other. The actual amount of increase or decrease in the yield cannot be estimated with any degree of accuracy. This method may, however, have some advantages for practical work as the "yield" is judged on the same basis as that on which the print is sold.

For a study such as this, it is necessary to be able to determine the actual amount of dye present on the fibers rather than the relative amount. Comparative methods do not make allowances for varying degrees of penetration into and through the fibers nor do they permit accurate determinations of the amount of dye that is lost during the various operations. To do this it is necessary to have some method of separating the dye from the fibers and determining the amount.

Estimates have been gathered from various sources as regards the amount of dyestuff that is lost in the print works. The minimum figure given was that twenty-five per cent was wasted. Other estimates ran up to seventy-five per cent. These serve to illustrate how little is actually known about the utilization of the dyestuffs. The average estimate of the loss is fifty per cent, that is, one-half of the dyestuffs purchased by the average print works is thrown away. The initial cost of the dyestuff is not the only loss occasioned by this wastefulness, although it is the main one. The costs of handling, preparing thickeners, removal of dyes from back greys, etc., must also be considered.

The great possibilities of increasing the efficiency of the entire process will more than compensate for any amount of time spent in a study of "color yields."

Work is being done in determining the actual efficiency of the printing process. The procedure for a single run will serve to illustrate the methods that are being tried. All this work is being done in cooperation with a local print works.

First, a pattern is selected in which the color to be studied is printed in an area that is well separated from other colors.

Second, the color must contain only a single dyestuff or a very simple combination of dyestuffs.

When a print is to be made which satisfies these conditions, the color is carefully made in the color shop and the amount used in the print room is determined by weighing the quantities sent out and returned. This does not take into account any losses that occur in the color shop. These losses are difficult to determine for single colors as they depend largely on the subsequent disposal of the color that is returned from the print room.

In the print room the following data must be obtained:

1. The amount of back grey printed in fitting the pattern.
2. The yardage of goods printed.
3. The width of engraving on the roller.
4. The width of the cloth being printed.
5. The amount of color spilled and left in the color trough.

From these data the amount of dyestuff actually printed on the cloth per repeat of the pattern may be calculated.

Samples of the print are collected directly after printing, after ageing, and after oxidation and washing. The amounts of dye on the fibers after each of these operations are determined and the loss during each treatment is calculated. The over all efficiency is given by the ratio of the amount of dye present after the final washing to the amount that was used in the print room.

Sufficient data have not been obtained at present to permit the presentation of conclusive results. The indications are, however, that a minimum of twenty-five per cent of the dye is lost. This figure is in agreement with the minimum estimate obtained from various printers.

The determination of the "color yield" is directly dependent upon the quantitative determination of dyes on the fiber. In the present study the simplest possible method, extraction with organic solvents and colorimetric comparison with standards, is being used. Many of the vat dyes can be extracted with pyridine and this solvent has been used quite successfully.

The standards used for comparison are prepared from samples of practically pure dyes. These contain none of the usual diluents and were furnished through the courtesy of the Du Pont and Ciba companies.

III. AGEING

The hydrosulfite ager has been in use for about fifty years in almost unchanged form. Practically the entire knowledge concerning it is that it consists of a box filled with steam and through which printed goods are passed to accomplish a certain result. It is supposed that during this operation the dye is reduced to the leuco form which is attracted to the fibers. It is known that heat is evolved during the process and that the lower the temperature at which the ager can be maintained, the greater will be the apparent "color yield," at least down to the boiling point

of water. That sums up almost our entire knowledge of agers.

It is quite generally recognized that the ageing process, little understood though it is, is the most important operation in printing. This is where the dye undergoes chemical reaction and local dyeing takes place. All the preceding operations are almost exclusively mechanical and are adjusted to satisfy whatever ageing condition may exist.

Numerous tests of a comparatively simple nature have been carried out in starting this study to gain a better understanding of the process. The results will be stated briefly. It has been found that:

1. Heat is evolved when cloth padded with glycerine is placed in an atmosphere of steam.
2. Heat is evolved when cloth padded with potassium carbonate is placed in an atmosphere of steam.
3. Heat is absorbed when the dyestuffs are reduced at 100° C.
4. The vapors in an ager contain only traces of sulfur dioxide and a little air. No formaldehyde is present under normal conditions.

The temperature within agers has been the subject of a great deal of general investigation. The source of the heat must be in the cloth itself so the maximum temperature must be present at this point. Therefore, in this study, measurements have been made as near this region as possible. This was done by sealing compounds of suitable melting points in very thin walled copper tubes. The tubes were then flattened and fastened to the cloth as it passed into the ager. This method has the disadvantage in that it indicates only the maximum temperature attained and the tubes have a considerable temperature lag. The results were, however, of interest in that they showed enormously higher temperatures than those measured by the ordinary methods. Typical readings were:

Temperature indicated at wall of ager.... 213° F.
Temperature indicated at center of ager... 234° F.
Temperature indicated by tubes ..... 245° F.

While the observation of the temperatures is of interest in showing the existence of such extreme conditions, the important thing is to be able to eliminate the heat. Many attempts have been made to dissipate the heat but the most logical solution of the problem would seem to be to prevent its formation. To do this it is necessary to have a complete understanding of the entire process. To obtain this information a very fundamental study of the various actions that may take place in an ager has been started.

Professor E. K. Strachan of Brown University and one of the senior students are cooperating with this project in making this study. An apparatus has been constructed to permit the direct measurement of the quantity of water taken up by cloth at varying temperatures and pressures so that a sample may be studied under conditions duplicating those occurring during ageing.

Known amounts of water and cloth are placed in a calibrated glass tube, over a column of mercury and the whole is surrounded by a bath to control the temperature. When the desired temperature has been attained, the pressure within the tube is adjusted to the desired value by raising or lowering the mercury level. The difference between the amount of water introduced and the amount in the vapor phase at equilibrium gives the quantity of water on the cloth. With a single sample, measurements may be made at a series of temperatures and pressures. Samples of printed cloth may also be studied.

The results of such measurements are not yet available but it is expected that these experiments will produce results that will lead to a better insight into ageing problems.

SUMMARY

The effects of various factors involved in the preparation of printing thickeners on the thickening value and "color yield" have been shown. Conditions for obtaining the most desirable results are described.

The effects of a variety of dyestuffs on the properties of the printing colors made with them have been illustrated.

A complete study of the efficiency of all the operations involved in printing has been started. Methods for making quantitative determinations of the amounts of dye fixed on the fibers are being investigated so that actual measurements of "color yields" can be made.

An apparatus has been constructed for making a detailed investigation of the various actions that occur during the process of ageing. The amount of water taken up under any possible conditions and the heat effect may be studied with either printed or unprinted samples of cloth.

Some Features of Crock Tests

WALTER C. DURFEE

THE danger connected with textile crock testing is that the requirements demanded of textiles will become too severe owing to an uncertainty as to what is reasonable in all cases and a desire to be on the safe side of this uncertainty so as to make manufacturing and commercial troubles beyond reason.

The good, connected with the testing, is that the manufacture of the textiles can be watched and the dyes and processes studied.

Some of the uncertainties on the commercial side seem to concern mainly the buyers who, with or without the aid of their test chemists, have to give consideration both to the wants of their trade and consideration to the expense of production.

On the manufacturing side, to avoid crock, there are countless details to be watched by the manufacturer and by those who cater to him.

The good judgment or discretion of the buyers and the fine carefulness of manufacturers and others tends to make demand of considerable improvement in methods of crock testing, as a relief and aid; so as to increase the certainty and accuracy—even though the old simple methods of test are still of great value and should never be forgotten. The keeping of records of crock tests appears to have become a useful practice and much record cloth of specified grade has been called for in response to announcements by Prof. L. A. Olney at the Lowell Textile Institute of Lowell, Mass. and a fairly steady demand for the association test machines has come to the W. C. Durfee Co. at 114 Federal St., Boston.

In addition to the details given in the Association Year Book 1935-6 (page 132 etc.) it has gradually become apparent that much attention should now be given to two items especially, first, the situation of the chemist in contact with the users of fabrics so that manufacturers and distributors can meet real situations and be free from imaginary situations, and secondly a perfecting of ways of using the crock records.

At present it would be a vague and dangerous guess for the writer to suggest for dresses 25 turnings of the test machine handle and for men's coats 8 turnings and some other test for pajamas and sweaters say ? and ? respectively or to suggest what test result is good. But the chemist specializing in textile testing who daily contacts the public can say what turnings represent usage or wear and what results cause protests. But saying this is awkward. It is "said" with samples, and apparently cannot be said with words. So there is a question how to make, explain, and name the records so that one can say something about them, discuss them, tabulate them, get the good from them. One circumstance bearing on this question has been noticed. It is that the amount of crock or stain on the record cloth seems to build up more rapidly and to stop accumulating sooner in the case of some dirty fabrics than in the case of some dyed fabrics:—so that by looking at a short test one can have an opinion about readily rubbed dirt and by looking at an additional more prolonged test have an opinion about some dyes, dyeings or dye processes. But in such matters one soon feels need for some way to be accurate and to have closer judgments and one wishes more and more care for as many good purposes as the care will permit.

Incidentally, as to care: the machine ordinarily remains uninjured. In case of doubt one marks the lower face of the bare test finger with a soft pencil and one places some emery cloth on the bed of the machine, to imitate cloth to be tested as much as possible. If then the pencil marks soon wear at all points as the machine is worked and the base of the machine is truly flat it is doubtless in good order. In any event, after a few turns on the said kind of cloth, this action should produce a resurfacing which should be correct unless the base of the machine has been altered from a flat condition. Lint is usually blown or knocked from the record cloth after each test. If nothing very crucial is in mind one takes no further precaution.

However it will be noticed that a bright light or shadow will warp the judgment when tests are being judged and to a slight extent it may make a difference what is near the record when it is viewed. It may perhaps even make a slight difference if the spot is held far or near so as to seem small or large and very likely it will seem to change if viewed very closely.

Therefore it is well to have a standard to compare. Such standards will have to be carefully kept or if records are freshly made from standard dyeings these dyeings will need to be kept extraordinarily free from accumulating dirt. So the question of proper light and proper standards is pressing. An investigation and some inquiries has led the writer to the practice of so holding the record or so adjusting the light that the record border appears neither shadowy or luminescent. A slight shadow is preferred to as light and confusing excess of light. When convenient a whitish background, unobstructed for some area, is preferred.

Now the next question,—after so having arranged to see the record in a fairly favorable light with a reference sample or two,—is the question,—"What intensity has the spot?" "How does it compare to the standard?"

Usually one can say more or less what the ratio of comparison seems to be. One can decide "Sample a little better, Sample O.K. etc., Sample about ¾ as prominent" etc. That is satisfactory very often. It is not very satisfactory to say that the spot is not worse than a very light gray or a slightly dark grey etc. etc., although some meaning could be made to go with such language, and it might do sometimes.

The No. 1, No. 2, No. 3 samples quoted by the Year Book are carefully chosen samples of severe—middling and very scant crock. They furnish a sort of reference system that seems to have little chance of furnishing difficulties and misunderstandings: since as standards or references or samples they are dyeings and to be compared with dyeings by people accustomed to dyeings.

However, many people seem likely to go without them, or fail to care for them, doubt their permanence or be uncertain about the light fastness of records made from them etc., etc., or balk at the expense of them even if small, or be confused in saying what is between a clear medium green-blue and a darkish deep blue.

As an alternative reference, samples of spots reproduced in porcelain are highly recommended as references probably available on sufficient demand.

For the moment it seems best however to attempt to have a reference scale of spots in some ordinary system even if it must be just some arbitrary spots to refer to.

It has been found, so far, that persons who have carefully seen a colored spot on white will willingly point out a corresponding spot in a light or dark grey or a black, on white, that seems to be equally intense, or perhaps equally "hungry" as they view the matter. Others will agree with them as a rule. This matching for density or intensity does not seem to interfere at all with an additional match for any definite duskiness seen in the sample, and does not interfere with still another match for the Munsell Value.

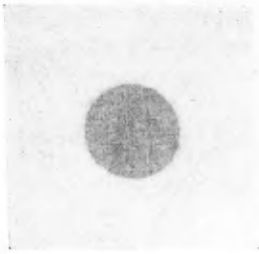


Fig. 1—"Crock" has long been explained as bad dyeing, dirt, etc. However, much that is rubbed off in a crock test is apparently fiber substance; loose or freshly loosened. The test cloth shown was rubbed on white wool many times and the invisible or white spot so obtained dyed with a wool dye with the result shown.

Accordingly, crock spots on white cloth are readily compared, regardless of color, to spots prepared in various greys on white provided attention is directed to the total depth of fullness of the shades, as seen when properly lighted on a white ground as before specified. The spots that seem most readily published are a selection of those used in printing.

It is expected to publish a set of printed spots in the Year Book of the Association when a good selection of spots can be tested out and properly graded.

Almost any good series of spots, graded by eye, will enable some laboratory work to proceed so that graphs can be made and records of comparisons.

A well regulated lighting method will be needed as many spots will tend to be considerably invisible in a light of their own color.

If the test cloth. in estimating the spots, is rotated to right and left slight changes will be noticed due to microscopic shadows from the warp and filling. Therefore the cloth should always be viewed in the same relative position.

Confusion in estimating spots on fabric can be lessened by viewing the test samples in a uniform manner such as by having the samples all squarely facing the eye and all in the same relative position to the light. The test samples can be improved when they are made by taking care to use the smooth face of the white rubbing test cloth and to rub this cloth in a direction oblique to its warp and filling.

A Bibliography of Mercerization

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EXPLANATORY NOTE

THE purpose of the authors in compiling this bibliography has been to assemble in one list the references to practically all of the journal articles on Mercerization and related subjects which have appeared since the publication of Mercer's original patent in 1850, to the end of 1935. No doubt some of the earlier articles have been overlooked but these would be of historical interest only at the present time.

All articles are grouped according to the year of their publication, and all those published in the same year are arranged alphabetically by their authors' names. The

reference to each article is followed wherever possible by a reference to an abstract of the article in some standard abstract journal. All titles of foreign articles are given in English.

References to patents have for the most part been omitted from this list, as they would have made the bibliography unnecessarily long, and most of the patents are entirely obsolete by now. If, however, any considerable demand for a patent bibliography should develop later, such a list could be readily compiled from the data already at hand.

There have been few books published on mercerization exclusively, but most of the standard text-books on the textile fibers and on dyeing have chapters devoted to this subject. For the convenience of those who wish merely to acquire a general knowledge of mercerizing, the following list of books, arranged chronologically, which is by no means complete, will perhaps be of some service.

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The Effect of Aniline Black on

Barium Activity Determinations

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UNDER "scouring procedure" in the method for the determination of barium activity numbers of dyed cotton AMERICAN DYESTUFF REPORTER, Vol. XXV, Page 188 (1936), it is recommended that after desizing, the material be boiled in a soap and soda ash solution. Unless cotton material dyed with aniline black is given this alkaline soap boil, the barium activity numbers of the material will be about 20% too high. This is due to the fact that most aniline black dyed material contains substances of acidic nature which neutralize some of the barium hydroxide, thus giving an apparent absorption of barium hydroxide higher than that due to the cotton alone. The alkaline boil neutralizes this acidic material and allows the cotton to show its true absorption. In order to make certain that all of the acidic substances in aniline black dyed cotton are neutralized, it is recommended that the cotton be given an additional boil for one hour in 1% sodium hydroxide solution.

The effect of alkaline treatment on aniline black material is shown by the barium activity numbers obtained on a sample of aniline black unmercerized cotton fabric.

Treatment	*Barium Activity Number*
Desized only	120
Desized and boiled in soap plus soda ash solution	103
Desized, boiled in soap plus soda ash solution, then in 1% sodium hydroxide, soured and rinsed	100

Progress Report

Methods of Determining Oil, Soap and Other

Extraneous Matter in Textile Materials

PROJECT 9-36

1—Investigation of the Nature of the Material Obtained by the Extraction of Wool with Ethyl Alcohol

BERTIL A. RYBERG*

INTRODUCTION

THE accepted method today for the determination of soap in wool makes use of ethyl alcohol as a medium for removing the soap from the wool. Trotman[1] extracts with petroleum ether to remove oils, then follows with hot absolute alcohol in a continuous extractor for three hours to remove the sodium and potassium soaps. Calcium and magnesium soaps are obtained by extraction with acidified ether. He further states that it is not possible to recover all of an added soap, the wool tending to retain some, particularly the alkaline portion.

King[2] also extracts with absolute alcohol for six hours, the temperature of the alcohol being as near the boiling point as possible. He also reports a deficiency of alkali in the extract, indicating that the wool retains part of the alkali. Krais and Biltz[3] also mention ether and alcohol for the "Estimation of Fat in Wool".

Neville and Harris[4] have shown that wool exhibits a pronounced selective adsorption of alkali from soap solutions. Woodmansey[5] in his work on the "Absorption and Retention of Soap by Wool", also found that the wool exhibited a preferential adsorption for the alkali.

Gilmore[6] seeking for a method of determining calcium soap on textile fibers, found that absolute alcohol tended to remove a greater amount of fatty acids than either benzene or carbon tetrachloride, but considerably less calcium than either of the other two solvents. He suggests the possibility of hydrolysis of the calcium soap in the presence of alcohol, the calcium hydroxide formed being strongly adsorbed by the wool or possibly insoluble in absolute alcohol, thus accounting for the deficiency of the base in the extract.

King[2] gives the following analysis of material obtained by extracting a special scoured flannel twelve times with absolute alcohol.

Total Extract	0.688%
Fatty Acids as Na Oleate	0.412
Sodium as Oleate	0.243
Saponifiables	0.418
Unsaponifiables	0.257
Calcium	Trace

The ratio of fatty acids to sodium as oleates $= \frac{.412}{.243}$ indicating that part of the alkali was retained by the wool. Another sample extracted twelve times (five to six hours) gave 1.14% of material, a further twelve extractions only 0.074%.

It has been fairly well established that wool, even when considered properly scoured, will always give at least 0.75 per cent to 1.00 per cent alcohol soluble material. In fact, many mill chemists have found that up to a one per cent of alcohol extract, preceded by ether, is allowable in manufacturing, without any serious difficulties. When

FOREWORD

For some time, textile chemists have known that wool when commercially cleaned contained from .05 to .2 per cent ether soluble material. This represents about the best practical scouring. After thorough extraction using ether, carbon tetrachloride, ethylene dichloride or other good oil solvents, a further .75 per cent to 1 per cent of material could be extracted using ethyl alcohol. The nature of this extract as far as we know, was not known, but rather much misinformation was prevalent regarding its composition.

Defective piece and yarn dyeing in the form of cloudy, streaky and irregular defects have always plagued the industry causing defective and second grade goods, expensive to the dyer. Impurities in wool when not evenly distributed are a cause of unsatisfactory dyeing. The alcohol extract following the other extractions has been suspected of causing trouble. In addition, the presence of an alleged impurity, in commercially clean wool, of an unknown nature, was a challenge. The work here outlined was undertaken to better understand wool, a valuable commodity. Our investigation is not complete and this paper is submitted as a preliminary report of progress.

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it begins to give more, it is an almost positive indication that the scouring process is faulty and serious difficulties will be almost certain to arise in further processing, particularly in piece and yarn dyeing. Raw stock and top may be dyed satisfactorily even in the presence of considerable impurities, but in piece and yarn dyeing, cleanliness is very important.

To our knowledge, this one per cent of alcohol extractable material has never been thoroughly investigated. That is, its composition definitely established. At present it is called soap. It is the opinion of the Sub-Committee on Methods of Determining Oil, Soap and Other Extraneous Matter in Textile Materials, of the A. A. T. C. & C., that a thorough investigation of the nature of the material obtained by the extraction of wool with ethyl alcohol, preceded by ethyl ether, would be a valuable contribution to the existing knowledge of wool and its impurities. We feel that it is misleading to call the total alcohol solubles, soap, especially in view of the fact that at least one per cent of alcohol solubles can be obtained from solvent scoured wool, which has never come in contact with soap at any time, with the exception of potash soaps occurring naturally in virgin wool.

The present method for determining soap in wool is at fault in that it removes other materials besides soap, which are called soap, also there is a deficiency of alkali. According to Von Bergen[7], oxidation such as takes place in ageing, reduces the amount of ether solubles, but increases the amount of alcohol solubles. Thus in many cases, oxidized oils are included in the alcohol extract as soap. There appears to be an overlapping effect between the ether and alcohol. The ether removing unoxidized oil, some oxidized oil, and some fatty acids from hydrolyzed soap. The alcohol removing oxidized oils, soap, higher alcohols, and free and esterified sterols such as cholesterol.

It is our purpose to investigate the alcohol soluble material obtained from wool in an attempt to determine its approximate composition, and as a result of this work, possibly develop a new, more accurate method for determining soap in wool.

MATERIALS

Two lots of fine Australian wool in top form, were obtained, having been prepared as follows:—

Lot 1. Wool cleaned from grease, etc., by the Solvent method, rinsed in warm water, carded and dry combed. This lot was prepared without using any oil, soap or alkali during processing, other than those naturally present in virgin wool.

Lot 2. This lot was prepared by the conventional method of scouring, using a Red Oil Soda soap and sodium carbonate. It was carded and combed with the addition of oil, then backwashed with a sulfated alcohol.

These two lots of wool, therefore, are representative of the two general methods used for cleaning wool.

Ethyl Ether, Anhydrous Analytical Reagent complying with the A. C. S. Specifications and containing not over 0.02 per cent alcohol.

Ethyl Alcohol, 95 per cent.

METHODS

The methods used in this work are in most cases modifications of existing methods, these modifications having been made in order to adapt them to the nature of the material being investigated.

PRELIMINARY WORK

The Effect of Moisture Removal by Oven Drying

Samples of the solvent scoured, lot 1, and the ordinary soap scoured, lot 2, wool top were oven dried at 105°-110° C. for 1½ hours. They were then transferred immediately to Sohxlet extractors and extracted for two hours (twelve extractions) with anhydrous ethyl ether. They were then oven dried again. The extract obtained was also oven dried and weighed.

The above experiment was repeated, this time using the wool top as is, that is, without oven drying.

Results

	Per Cent Ether Extract	
	Oven dried	As is
Lot 1 (Solvent Processed)	0.66	0.76
Lot 2 (Soap Processed)	0.84	0.94

The above results are based on oil and grease free oven dried material.

The oven dried, ether extracted samples were further extracted, this time with 95 per cent ethyl alcohol for 6 hours (12 extractions). The material obtained by this extraction was oven dried and weighed.

Results

	Per Cent Alcohol Extract	
	Oven dried	As is
Lot 1	1.17	1.25
Lot 2	1.24	1.12

These results also based on oil and grease free oven dried material.

A further extraction was made with ethyl ether acidified with formic acid, in order to determine Calcium and Magnesium soaps.

Results

	Per Cent Fatty Acids	
	Oven dried	As is
Lot 1	0.09	0.03
Lot 2	0.05	0.10
Totals of all extractions		
Lot 1	1.92%	2.12%
Lot 2	2.12	2.15

A survey of the results obtained indicates that oven drying previous to extraction, has a noticeable effect on the amount of material removed by the ethyl ether, less being removed than when the material is not dried. The alcohol extraction tends to even up the difference, the total sum of ether plus alcohol being practically the same whether dried or not, particularly in the case of soap scoured wool. These results tend to substantiate the work of von Bergen[7].

Since we are interested in the alcohol solubles, it was decided from the results given above, to use wool without oven drying in order to obtain the truly alcohol solubles.

The low results obtained by extraction with acidified ether indicates that good, soft water was used in processing the wool.

Preliminary Removal of Residual Oils and Grease

The wool was prepared for the alcohol extraction by extracting twelve times with anhydrous ethyl ether in a battery of Sohxlet extractors.

The wool was thoroughly air dried, then replaced in the extractors and extracted twelve times with 95 per cent ethyl alcohol.

In order to obtain enough of the alcohol extractables for a thorough investigation of their nature, it was necessary to extract a large amount of wool, approximately ten pounds of each lot being used.

The alcohol extracts obtained were dried several hours at just below the boiling point of ethyl alcohol, that is, about 70°-75° C.

In sampling, it was felt that the material should not be oven dried to constant weight, since the possibility of losing volatile parts of these extracts, exists. Also the heat may accelerate oxidation, which is also possible, thus changing the characteristics of the material in question. In order that this material shall always be under the same conditions, it was placed in a desiccator containing sulfuric acid in such concentration as to maintain 45 per cent relative humidity, which is an average of the extremes in the conditions of the laboratory.

ANALYTICAL WORK

Determination 1

Free Fatty Acid

Duplicate samples were taken, to which were added 50 ml. of neutralized 95 per cent ethyl alcohol, 3 to 4 drops of phenolphthalein and the whole brought to a boil. This alcoholic solution was then titrated with 0.0200 N sodium hydroxide solution until a pink color permanent for 1 minute was obtained.

Results	Lot 1	Lot 2*
Free Fatty Acid as Oleic	31.9%	12.4%

2

Total Organic Matter Extractable with Ethyl Ether After Treatment awith Hydrochloric Acid

Samples of the alcohol extracts were placed in beakers and treated with 50 ml. portions of ether and as much of the material taken up in the ether as possible. The ether was then transferred to a clean dry separatory funnel. The process was repeated until most of the material in the beaker had been transferred to the separatory funnel. After as much material as could be removed, had been taken out by the ether, 50 ml. distilled water and 10 ml. of hydrochloric acid solution were added and the beaker heated to boiling. After cooling somewhat the contents of the beaker were also transferred to the separatory funnel. The process was repeated, interposed with additional ether treatments until all of the material in the beaker had been transferred to the separatory funnel.

The funnel was then stoppered, thoroughly shaken and then permitted to stand until the layers had separated. The water layer was drawn off into one beaker and the ether layer into another. The aqueous solution was then returned to the funnel and treated with fresh ether. The two ether portions were then combined in the separatory funnel and fresh water was added in order to wash out the acid. At this point a difficult situation arose. An extremely persistent emulsion formed between the ether and water layers, at times holding nearly all the water.

This emulsion made it very difficult to wash out the acid from the ether layer, particularly since the aqueous extracts were to be saved for the determination of any metals present in the original sample, thus making it impossible to use any other material (salt) to break the emulsion. This emulsion was drawn off into another separatory funnel for further treatment. The ether layer was washed with successive portions of distilled water until neutral. Whenever an emulsion occurred it was drawn off and added to the first emulsion. These emulsions so collected, were treated alternately with ether and water until neutral to methyl orange and the emulsion itself reduced considerably in volume. However, it was found impossible to break it entirely. The neutral emulsion was drawn off into a beaker and the ether added to the first ether extract and evaporated down carefully. The emulsion was also carefully evaporated to dryness, then treated with ether again, this ether extract being added to the first.

The total ether extract was evaporated and then dried on the water bath to constant weight.

Results	Lot 1	Lot 2
Total Organic Matter Soluble in ether after acidification	62.9%	58.8%

3

Total Fatty Acids

The residue from the total organic matter determination (2) was taken up in 50 ml. of neutralized 95 per cent alcohol and 3-4 drops of phenolphthalein added. It was brought to a boil, then titrated with 0.0200 N sodium hydroxide solution until the pink color obtained is permanent for one minute.

Results	Lot 1	Lot 2
Total Fatty Acid as Oleic	26.5%	27.2%

Combined Fatty Acid as Oleic

Total Fatty Acid—Free Fatty Acid=Combined Fatty Acid

In the case of solvent scoured wool, the Total Fatty Acid obtained was less than the Free Fatty Acid indicating that there apparently was no Combined Fatty Acid.

The yield of total fatty acid obtained being lower than the free fatty acid is attributable somewhat to the extreme difficulty experienced in obtaining the total organic matter, due to the formation of the emulsions. The presence of oils and waxes appear to be the cause of the

*The results given are based on the alcohol extract as being 100%.

emulsion formation since a waxy substance was obtained by evaporation of the emulsion portion, which was only partially soluble in neutral ether.

	Lot 2
Combined Fatty Acid	14.8%

In the case of lot 2 some of the fatty acid exists in the combined state.

Oils and Waxes Soluble in Ether

Oil and Wax=Total Organic—Total Fatty Acid

	Oil and Wax
Lot 1	31.0%
Lot 2	31.6%

Determinations for total organic and total fatty acid were repeated, this time heating the acidified samples under a reflux until the fatty material had separated and come to the top in a clear layer. The solution was cooled, transferred to a separatory funnel and treated with ethyl ether. In this case only a small amount of emulsion was formed which was easily taken care of.

Results	Lot 1	Lot 2
Total Organic Matter (Det. 2)	64.3%	61.7%
Total Fatty Acid (Det. 3)	27.9	28.9
Combined Fatty Acid (Diff.)	00.0	16.5
Oils and Waxes	32.4	32.8

It is believed from observations, that some of the fatty acids are very volatile and that some of them are lost during the determination of the total organic matter, since solvent scoured wool shows a total fatty acid which is less than the free fatty acid. However, this is only an assumption.

The use of aqueous sodium hydroxide in the determination of freey fatty acid was questioned, so the work was repeated using alcoholic potassium hydroxide.

Results	Lot 1	Lot 2
Free Fatty Acid (Alcoholic KOH)	32.8%	11.3%

Metals in the Acid Aqueous Extract

The combined aqueous extract and washings from the total organic matter determination (2) was heated in a watch glass covered beaker on the water bath until all the ether had been driven off. The volume of the solution was reduced to approximately 200 ml. by evaporation, cooled and transferred to a 250 ml. volumetric flask and made up to the mark with distilled water.

Iron and Aluminium

The acid aqueous solution (100 ml. of the above solution) was brought to a boil, a few drops of bromine water added and the boiling continued for a few minutes to drive off the excess bromine. Concentrated ammonia was added with stirring until the solution became definitely ammoniacal. It was boiled 2-3 minutes, then allowed to stand a few minutes. This test proved to be negative, meaning there was no iron or aluminium present.

Calcium Oxide

The solution remaining from the iron and aluminium determinations was heated to boiling and 10 ml. of ammonium chloride solution and 10 ml. of saturated ammonium oxalate solution were added, followed by sufficient concentrated ammonia to make the solution definitely ammoniacal. After thorough stirring, the whole was then digested for one hour on the water bath. This test also proved to be negative.

Magnesium Oxide

The solution remaining from the calcium oxide determination was warmed and 10 ml. of sodium ammonium phosphate solution were added slowly with constant stirring. This was followed by 25 ml. of concentrated ammonia solution. The covered beaker was allowed to set four hours or more before filtration. This determination showed only a slight trace of magnesium oxide which might be due to impurities in the chemicals used.

Potassium Oxide

Another 100 ml. portion of the acid aqueous solution from the total organic matter determination (2), was evaporated to dryness, the residue then taken up with hot water and filtered to remove some of the organic matter. The solution was then brought to a boil, acidified with hydrochloric acid and a slight excess of barium chloride was added to remove sulfate ion which interferes with the determination of the potassium oxide. It was allowed to stand over night, then filtered, the precipitate washed and the filtrate plus washings were made alkaline with ammonia. Ammonium carbonate was added until no further precipitate was formed, and also a few drops of ammonium oxalate. It was filtered and washed. The filtrate was carefully evaporated to dryness in a casserole, then heated just below redness till all of the ammonium chloride fumes were gone. It was cooled, the residue dissolved in 25 ml. of hot water and filtered to remove organic matter. One ml. of 60 per cent perchloric acid was added, then it was evaporated until nearly dry and when heavy fumes of perchloric acid appeared, it was cooled. Hot water, perchloric acid, etc., treatments were repeated. When cool 35 ml. of alcohol were added and the whole filtered on a fritted glass crucible, washing with alcohol, drying and weighing.

Results	Lot 1	Lot 2
Potassium Oxide	6.42%	1.86%

Sodium Oxide

Another portion of the acid aqueous solution was placed in an Erlenmeyer flask and evaporated to dryness on the water bath. The residue was taken up in the smallest portion of water possible (15 ml.). It was filtered to remove organic matter and the filtrate and washings were reduced to 15 ml. Magnesium uranyl acetate reagent was added in excess, the number of ml. of reagent added being 10 times the number of mg. of sodium oxide present. The flask was partially immersed in water whose temperature was under 20° C. and the solution was vigorously stirred with a motor stirrer for 30-45 minutes. The precipitate was then immediately filtered into a weighed fritted glass crucible using gentle suction. The beaker and precipitates were washed with 95 per cent alcohol, the crucible then dried at 105°-110° C. for 30 minutes.

Results	Lot 1	Lot 2
Sodium Oxide	0.00%	4.73%

Sulfur as Sulfate

Another portion of the acid aqueous solution was made strongly acid with hydrochloric acid, heated to boiling and barium chloride added in slight excess. It was allowed to stand over night, then filtered, washed, dried, ignited and weighed as barium sulfate.

Results	Lot 1	Lot 2
Sulfur as sulfate	0.71%	0.38%

Chloride Ion

A sample of the alcohol extract was digested for one hour with concentrated sulfuric acid, potassium sulfate and copper sulfate as in a typical Kjeldahl digestion in order to destroy the organic matter. The digest was taken up in considerable distilled water, the sulfate ion removed by the usual method, and the chloride ion precipitated with silver nitrate.

Results	Lot 1	Lot 2
Chloride Ion	0.87%	0.84%

Ash

Samples of the alcohol extract were ashed directly in platinum.

Results	Lot 1	Lot 2
	9.72%	10.86%

Calculated Distribution of Salts in the Ash

	Lot 1	Lot 2
Potassium sulfate (K_2SO_4)	1.29%	0.69%
Potassium carbonate (K_2CO_3)	8.41	2.19
Sodium Carbonate (Na_2CO_3)	—	8.09
Total	9.70%	10.97%
Ash	9.72	10.86
Error	0.02	0.11

$$\frac{.02}{9.70} = .2\% \qquad \frac{.11}{10.86} = 1.0\%$$

Protein Matter (Nitrogen)

Samples of the alcohol extract were analyzed for nitrogen by the Micro-Kjeldahl method through the cooperation of Milton Harris, A. A. T. C. & C. Research Associate at the Bureau of Standards.

Results	Lot 1	Lot 2
Nitrogen	2.12%	1.40%

When these results are converted into protein content, they show 12.7 and 8.4 per cent, respectively, assuming this protein to have the same nitrogen content as wool itself (16.60 per cent).

Saponification Number

Fifty ml. portions of alcoholic potash solution were added to samples of the alcohol extract, contained in refluxing flasks. Blanks were also prepared. The flasks were heated for 1 hour in a steam bath with frequent agitation, then cooled and titrated with standard acid plus phenolphthalein.

Results	Lot 1	Lot 2
Saponification Number or mg. KOH/g sample	94.4%	51.5%
Sap. No. expressed in terms of Oleic Acid	47.2	25.8
Sap. No. as oleic minus free fatty acid as oleic = Saponifiables other than fatty acid in terms of oleic	14.4	14.5
Unsaponifiables based on Oleic (Diff.)	52.8	74.2

The high percentage of unsaponifiables particularly in the case of the soap scoured wool (2) points to the presence of higher alcohols and free sterols such as cholesterol and iso-cholesterol.

Iodine Number

One-quarter gram samples of the alcohol extracts were weighed into wide mouthed glass stoppered flasks. Fifteen ml. of chloroform were added to each followed by 25 ml. of Hanus solution. The stopper was moistened with 15 per cent potassium iodide solution. They were allowed to stand 1 hour, then 20 ml. of 15 per cent iodide solution and 100 ml. of freshly boiled and cooled water were added and the whole titrated immediately with 0.1 N thiosulfate. Blanks were made with each determination.

Results	Lot 1	Lot 2
Iodine Number	52.3	46.3

The iodine number obtained further indicates the presence of cholesterol whose iodine number is 68.8.

Since cholesterol is known to be present both in wool itself (H. C. Eckstein[8]) and in wool grease, it was assumed to be present in the alcohol extract also. Cholesterol is readily soluble in hot or boiling alcohol, but only slightly soluble in cold alcohol. The cholesterol or mixture of sterols, were determined according to the method of Windaus[9], using digitonin to form the cholesteride. The method is as follows:—

A sample of the alcohol extract was taken up in thirty times its volume of hot ninety-five per cent alcohol. This solution was treated with a one per cent solution of digitonin in hot ninety-five per cent alcohol, as long as a precipitate was produced, being sure to add a slight excess. After several hours the precipitate was filtered on a fritted glass crucible and washed first with alcohol, then ether. It was dried at 100°-105° C. and weighed.

Results	Lot 1	Lot 2
Cholesterol	11.3%	10.9%

Tabulated Results of an Examination of the Material Obtained by the Extraction of Wool with Alcohol Preceded by an Extraction with Alcohol Free Ethyl Ether

Results	Lot 1	Lot 2
1. Free Fatty Acid as Oleic. (NaOH)	31.9%	12.4%
Free Fatty Acid as Oleic. (Alcoholic KOH)	32.8	11.3
2. Total Organic Matter Extractable with Ethyl Ether after Acidification with HCl	62.9	58.8
Number 2 refluxed during heating	64.3	61.7
3. Total Fatty Acid as Oleic.	26.5	27.2
Total Fatty Acid as Oleic. (Refluxed)	27.9	28.9
4. Combined Fatty Acid as Oleic.	00.0	14.8
Combined Fatty Acid as Oleic. (Refluxed)	00.0	16.5
5. Oils and Waxes Soluble in Ethyl Ether.	31.0	31.6
Oils and Waxes Soluble in Ethyl Ether (Refluxed)	32.4	32.8
6. Iron and Aluminium	Absent	Absent
7. Calcium as CaO	Absent	Absent
8. Magnesium as MgO	Trace	Trace
9. Potassium as K_2O	6.42	1.86
10. Sodium as Na_2O	0.00	4.73
11. Sulfur as SO_4	0.71	0.38
12. Chlorine as Chloride Ion	0.87	0.84
13. Nitrogen by Micro-Kjeldahl	2.12	1.40
14. Protein based on Nitrogen Content of 16.60%	12.7	8.40

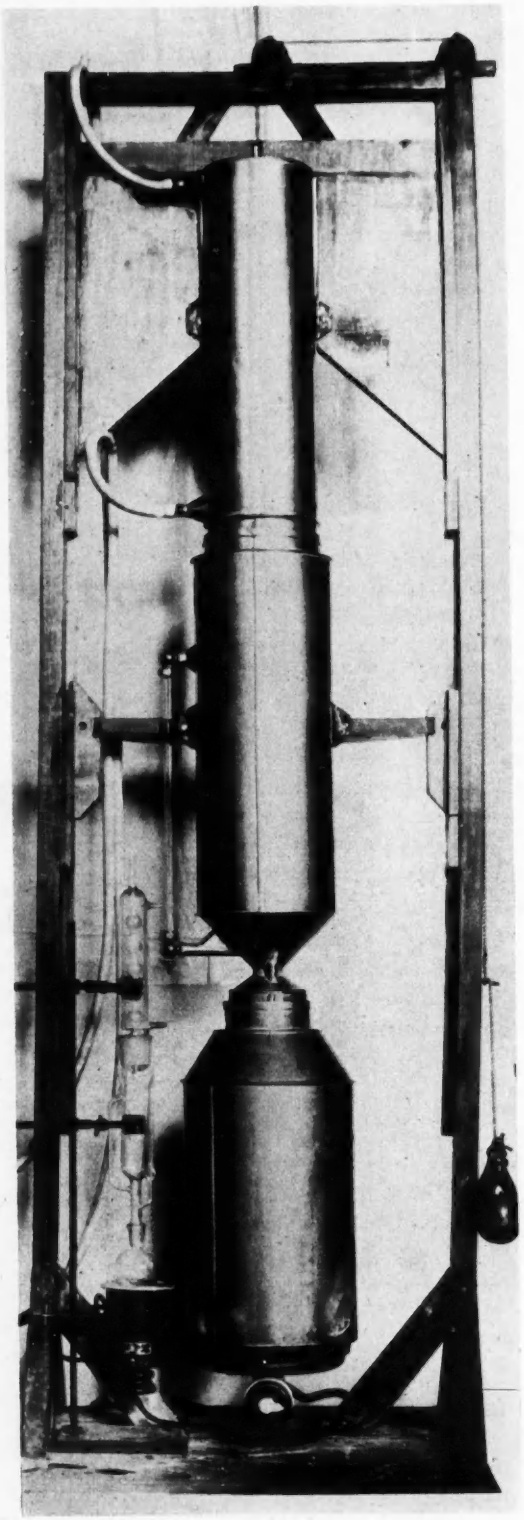

Fig. 1

15. Ash in Platinum	9.72	10.9
16. Saponification Number	94.4	51.5
17. Saponifiables as Oleic	47.2	25.8
18. Unsaponifiables by difference, including soap	52.8	74.2
19. Saponifiables other than Free Fatty Acids calculated to Oleic	14.4	14.5
20. Iodine Number	52.3	46.3
21. Cholesterol or Sterols	11.3	10.9

Composition of Alcohol Extracts by Analysis

	Lot 1	Lot 2
Free Fatty Acids calculated as Oleic	32.8%	11.3%
Combined Fatty Acids as Soaps	00.0	16.5
Saponifiables other than Free Fatty Acids	14.4	14.5
Unsaponifiables (not including combined fatty acid)	52.8	57.7
Totals	100.00	100.00

Further investigation is being made into the composition of the unsaponifiables and the saponifiables other than

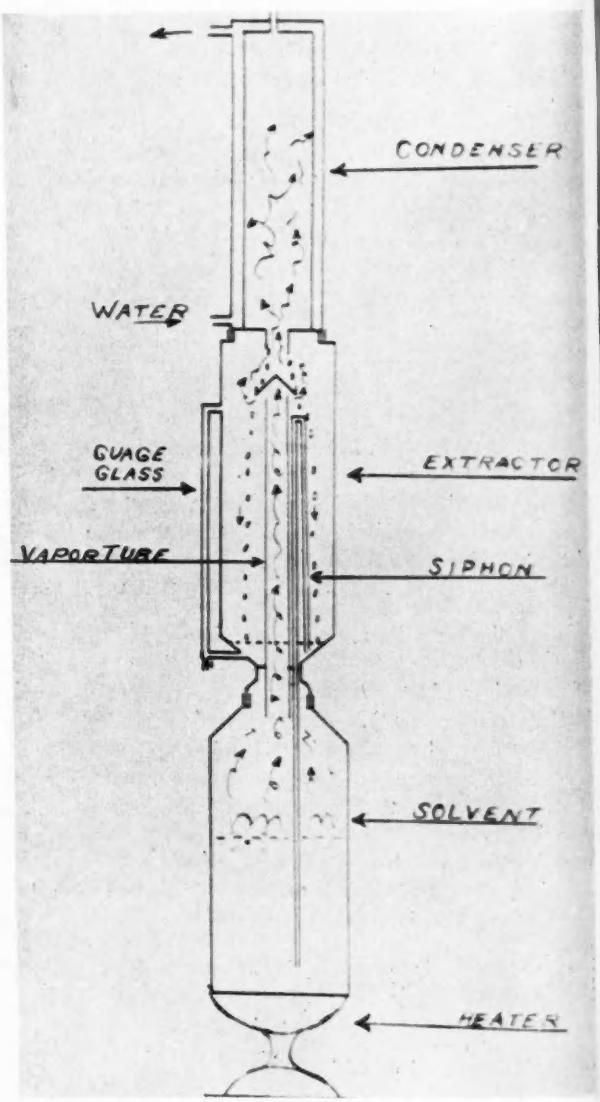

Fig. 2

free fatty acids. It is hoped that the components of the unsaponifiable portion can be separated and identified.

The alcohol soluble materials used in this investigation were obtained by a large number of extractions made on a small scale. Under these conditions the material was exposed to boiling alcohol for a considerable length of time, and it is reasonable to believe that the product finally recovered might differ in composition from that obtained in a single extraction.

In order to overcome this condition and yet obtain enough material for a thorough investigation, the associate designed a Sohxlet extractor capable of holding six pounds of wool, which is one hundred times the capacity of the 250 ml. size glass Sohxlet.

Figure 1 is a photograph of this extractor compared to a 250 ml. glass extractor. This large apparatus is made of Monel metal and is separable into three parts. Figure 2 shows a cross-sectional diagram of it, indicating the various parts and the scheme of operation. It differs from the conventional Sohxlet in that the vapor tube passes up through the center of the extractor and the siphon also is contained within it. It is fitted with a gauge glass in order that the progress of the extraction may be followed.

The condenser was designed as such in order that a large amount of condensing surface be available for use with extremely low boiling solvents such as ethyl ether.

The syphon tube was extended to within two inches of the bottom of the reservoir in order that it be continuously sealed and thus assure proper syphoning in a minimum of time.

More of the two types of wool top were obtained for use in this large extractor. The time cycle for a complete filling of the extractor with fresh solvent and also emptying, was found to be approximately three times that required by the conventional 250 ml. glass Sohxlet.

At the present time sixteen pounds of lot one and twelve pounds of lot two have been successively extracted with anhydrous ethyl ether and ninety-five per cent ethyl alcohol and the extracts recovered.

This material will be examined in much the same manner as given in the first part of this paper. In addition to this, fractional crystallization will be attempted in an effort to separate the substance into several of its components, each of which will be further recrystallized and a number of constants such as specific rotation in various solvents, melting point, etc., be determined, in order that they may be partially identified.

The final results of this investigation of the alcohol extract obtained from wool, will be available in the near future and will, we feel, be a distinct contribution to the existing knowledge of the behavior of wool during processing.

ACKNOWLEDGMENT

This investigation was made possible by a grant from the Textile Foundation to the American Association of Textile Chemists and Colorists. We wish to express our appreciation for the aid given.

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